Volume 41 January, 1936 Number 1

SOIL SCIENCE

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Published Monthly by THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES, BALTIMORE, MARYLAND, U. S. A.

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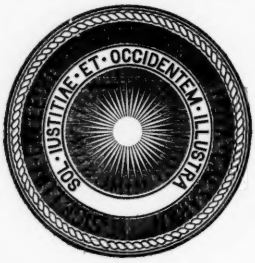
SOIL SCIENCE



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STATIC FRICTION MEASUREMENTS IN THE STUDY OF SOIL MOISTURE RELATIONSHIPS[1]

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Received for publication April 15, 1935

The relationship between soil particles and the water films that surround them has always interested soil scientists. The layers of water that surround the individual particles of the soil are obviously bounded by two kinds of interfaces: the inner one, a phase boundary between a solid and a liquid; and the outer one, a phase boundary between a liquid and a gas. Although there is some information available concerning the activity of surface tension forces at the air-water interfaces in soils, little is known about the active forces at the water-soil interface, which must be of molecular character and which are probably of relatively great magnitude. The distance through which such forces act at the latter phase boundary and the possibility of discontinuity at certain points in the moisture range are of especial interest.

REVIEW OF LITERATURE

The dilatometer studies of Bouyoucos (3) seemed to indicate that there is an abrupt change in the characteristics of water a short distance away from the solid-liquid interface in a soil-water system. Below a certain point in the temperature scale it was found impossible to freeze any more water in wet soils. The amount of this unfree water varied with the amount of internal surface, clays holding much more water against the freezing processes than did sandy soils. Bouyoucos has suggested that this unfreezable water is no longer in the liquid state but exists as water of hydration or water in solid solution. This is not necessarily true, since the formation of ice crystals merely requires a rearrangement of water molecules in a definite crystal lattice pattern, a process which may be easy in the absence of restraining forces but probably difficult if the water molecules are already oriented and strongly held at a solid-liquid interface. When the force of attraction and orientation is greater than the force of crystallization, it is probable that no more ice crystals will form.

Vapor pressure measurements within a soil made by Edlesfson (5) and others seem to indicate a discontinuity and an abrupt change in state a short distance from the interface because vapor pressure is at maximum value over a long

[1] Published as Scientific Paper No. 308, College of Agriculture and Experiment Station, State College of Washington.

range in soil moisture and then suddenly drops to about zero near the wilting point.

Atterberg's studies (1) indicated rather abrupt changes in the consistency of clays when the moisture content was varied. Abrupt color changes often occur as clays dry out.

During the war, Hardy and Hardy (7) made extensive studies of the ability of different liquids to overcome friction. They used several organic liquids, including acids, and water and studied their effect on the friction between glass surfaces. They found that water was not a good lubricant even when flooded on such surfaces. The more strongly polar compounds were most active in overcoming friction. Hardy used measurements of static friction rather than measurements of moving friction because of the simplicity resulting from the important fact that the coefficient of static friction is entirely independent of the area in contact. This seemed to commend the measurement of static friction in connection with soil investigations where exact surface areas are usually difficult to ascertain.

Soon after Hardy's work appeared, Crowther and Haines (4), of the Rothamsted Experimental Station, reported studies in which they placed a negative charge on plow mold boards, which resulted in a movement of water to the metal-soil junction and reduced the drawbar pull through reduced friction with the soil. Laboratory studies of sliding friction between metal surfaces and moist soils were also made, which agreed with the field experiments. In these studies it was found that the higher the moisture content of the soil, the greater was the reduction in kinetic friction due to the electric charge.

Baver (2) reported work with the coefficient of kinetic friction at various moisture contents and showed the relationship of these values to the Atterberg constants. He concluded that the upper plastic limit of Atterberg corresponds to the point of maximum adhesion. Atterberg, however, determined the point of maximum adhesion and found that it occurs in the range of moisture between the upper and lower plastic limits, a point which he termed the "sticky limit."

The determination of coefficients of static friction at different moisture percentages appeared to be a unique means of studying the question of soil-water relationships, and, since there is obvious disagreement about the nature of the moisture films at the solid-liquid interface in moist soils, the experiments reported here were undertaken.

SOILS

Six clays were selected for study. They were obtained from widely separated points and were representative of at least three types of soil formation. In order to eliminate the effects of organic matter as much as possible, samples of deep horizons were used. The percentage of clay smaller than 0.002 mm. in diameter was determined by the Robinson pipette method. Atterberg constants were found according to the directions of this investigator. The

colors were checked against Ridgeway's color standards, table 1 shows the results.

A chemical analysis was made of sodium carbonate fusions according to the usual methods, and sodium and potassium were determined directly from J. Lawrence Smith fusions, using the zinc-uranyl acetate method and the cobaltinitrite method respectively. The results, together with calculations of the silica sesquioxide ratio, are given in table 2.

TABLE 1

Some physical characteristics of the clays used

SOIL	LOCALITY	COLOR*	CLAY CONTENT	ATTERBERG CONSTANTS		
				Rolling limit	Flow limit	Plasticity number
			per cent	*per cent*	*per cent*	*per cent*
Fortuna	Honduras, C. A.	Ferruginous	53.0	35.9	53.4	17.5
Spur Tree	Jamaica, B. W. I.	Morocco red	†	39.1	43.1	4.0
Hagerstown	Hagerstown, Pa.	Cinnamon rufous	56.0	28.7	54.8	26.1
Cecil	Rockville, Md.	Apricot orange	48.0	36.2	47.7	11.5
Napanee	Ypsilanti, Mich.	Pale smoke gray	57.0	20.7	36.4	15.7
Kalispell	Cusick, Wash.	Gull gray	66.0	38.2	67.1	28.9

* From Ridgeway.

† Dispersion not successful.

TABLE 2

Chemical analysis of the clays used

SOIL	RATIO $\frac{SiO_2}{R_2O_3}$	PERCENTAGE						
		SiO_2	Al_2O_3	Fe_2O_3	Ca	Mg	K	Na
Fortuna	2.50	51.94	31.95	5.20	0.40	1.08	0.43	0.34
Spur Tree	0.10	3.98	61.10	10.10	0.90	0.62	0.18	0.44
Hagerstown	3.20	57.93	27.40	5.20	1.01	1.74	0.97	0.50
Cecil	3.07	57.19	27.50	6.40	0.50	1.45	2.30	0.51
Napanee	5.25	44.79	12.70	2.80	9.70	3.24	2.27	0.79
Kalispell	4.90	65.05	20.03	3.40	1.30	2.46	2.04	1.06

MEASUREMENTS OF STATIC FRICTION

The method of Hardy and Hardy was employed except that shallow pans filled with moist soil were substituted for the lower glass plate. A new watch glass about 6 cm. in diameter and perfectly smooth on the bottom was fitted with a hook on the upper side, extending to the edge of the glass. One end of a piece of silk thread was attached to the hook, and the other end was fastened to a balance pan. A beaker support was attached to a ring stand with a short upright, and opposite to the beaker support was placed a rod having a metal

wheel at the end. The wheel was almost frictionless and was adjusted in such a manner that the silk thread extending over it to the watch glass when resting on the soil was parallel to the soil surface. Metal pans 8 cm. in diameter and 0.4 cm. deep were filled evenly with thoroughly wetted and mixed soil, and the surface was smoothed with a spatula. The pans were placed on the beaker support, which was perfectly level when measurements were being made.

In making a measurement the pan of soil was placed in its support after the surface had been carefully smoothed, and the watch glass loaded with 30–40 gm. of metal shot was carefully placed on the soil. The silk thread was laid over the metal wheel so that the balance pan, hanging over the edge of the table, was above a support placed about 1 inch below the pan. Shot was then slowly added to the balance pan until the watch glass just started to move. Since static friction is always greater than moving friction, the glass rapidly moved over the soil once it had started. The object of the experiment was to add only enough shot to start the glass moving. A fraction of a gram less than this weight is the true value to be sought. This is spoken of as the "threshold value" and represents the force necessary just to overcome the force of static friction. The test being completed, both watch glass with shot and balance pan with shot were weighed and the data recorded. The soil was again smoothed, the watch glass with a larger load of shot replaced in position, and the process repeated. A third trial with a larger load of shot, preferably about 100 gm., was made. When this reading was obtained, duplicate samples of the soil near the center of the plate were taken out and placed in weighed dishes with tight covers for moisture determinations. These samples, after being weighed, were dried in an oven at 105°C. and then reweighed. Moisture percentages at the time of the friction determinations were then calculated, the percentage being based on the weight of ovendried soil.

The coefficient of static friction (U) is calculated from the relationship $U = \frac{P}{L}$, where P is the weight required just to start the load (L) moving on a plane surface. The value of U is always less than unity (8). Because the amount of surface area in contact has no effect on this coefficient, the ratio $\frac{P}{L}$ is a linear function for a given pair of surfaces, and it is possible to standardize the load at any convenient point along the curve. For these experiments a standard load of 100 gm. was selected. The nature of the linear curves obtained with a sample of Hagerstown clay is shown in figure 1. The corresponding moisture content is shown with each set of determinations. It will be noticed that the slope of the curve is not always the same but that the experimental points are always in linear relation. The coefficient of static friction with any load can be read from these curves.

Storage of the thin plates of soil in an enclosed desiccator of large size, but

without any drying substance in it, resulted in a gradual loss of moisture from the soil; but capillarity maintained a uniform moisture content from top to bottom of the plate. After suitable periods of time, when an appreciable loss in moisture had occurred, new measurements were made. By starting the experiment with very moist samples and allowing the soil to lose water slowly,

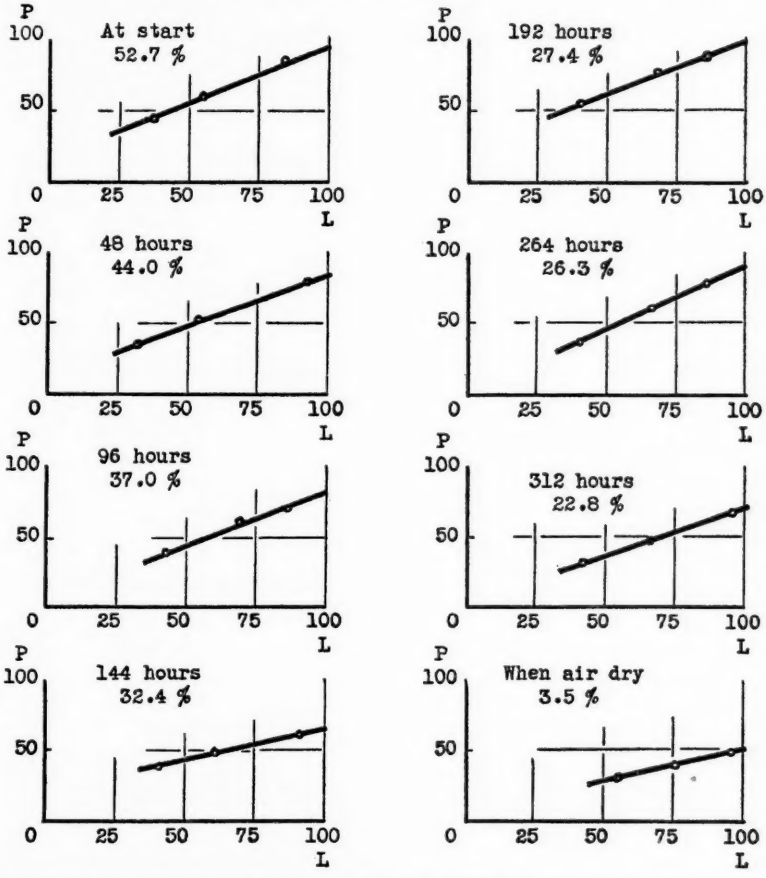

FIG. 1. THE LINEAR RELATION BETWEEN THE PULL (*P*) AND THE LOAD (*L*) IN STATIC FRICTION MEASUREMENTS AT DIFFERENT MOISTURE PERCENTAGES IN HAGERSTOWN CLAY

a series of measurements along the entire moisture range was made on the same plate of soil. As samples are removed, the soil may be worked to one side of the plate for smoothing and testing. The time required for a complete run from very moist soil to the air-dry condition varied with different soils. That for Hagerstown clay is indicated in figure 1.

EXPERIMENTAL RESULTS

The variations in the coefficient of static friction with changing moisture contents in six clays are shown by means of graphs (fig. 2, 3, 4). The coefficient of static friction is shown as the dependent variable, and the moisture content as the independent variable. The Honduras and Jamaica soils are shown together in figure 2, since both are lateritic soils and the latter may be a true laterite. Figure 3 shows the results with the Cecil and Hagerstown clays, both of which are residual soils. Results with two glacial soils as represented by the Napanee and Kalispell clays are shown in figure 4.

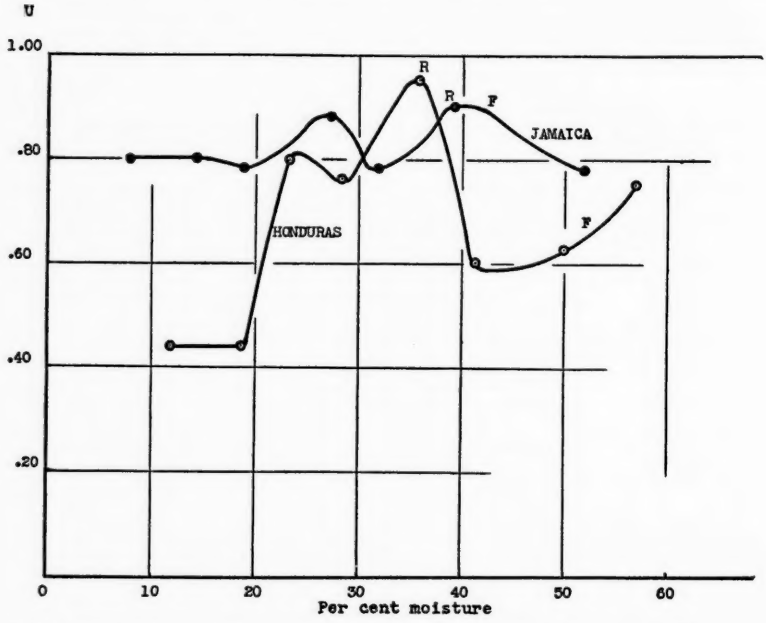

FIG. 2. CHANGE IN THE COEFFICIENT OF STATIC FRICTION WITH INCREASING MOISTURE CONTENT OF THE HONDURAS AND JAMAICA CLAYS AND THE RELATIONSHIP OF THE CURVES TO THE ATTERBERG CONSTANTS

R and F represent rolling and flow limits respectively

It will be observed that in all cases the coefficient of static friction increases to a maximum value after passing a moisture content that closely corresponds to the wilting point as determined by separate studies according to the Bouyoucos method, drops to a low point, and then gradually rises again. In some cases a sub-maximum value was indicated. The rolling limit was found to correspond to the point of maximum friction in every case. The flowing limit is not definitely associated with any particular point on the friction curve but tends to fall near the beginning of the second rise in the curve. It should be

noted that, after the flowing point is passed, the soil particles are free to move over one another and the loaded watch glass sinks into the moist clay and meets with a mechanical resistance similar to that of plowing. The wetter the soil becomes, the deeper the glass sinks and the greater is the resistance to movement. Consequently, a rise in the curve after passing the flowing limit is not a true measure of friction at these moisture percentages. It is more than likely that the friction constantly approaches a very low value as the soil becomes more and more liquid, since the friction of glass on a pure liquid surface is comparatively low.

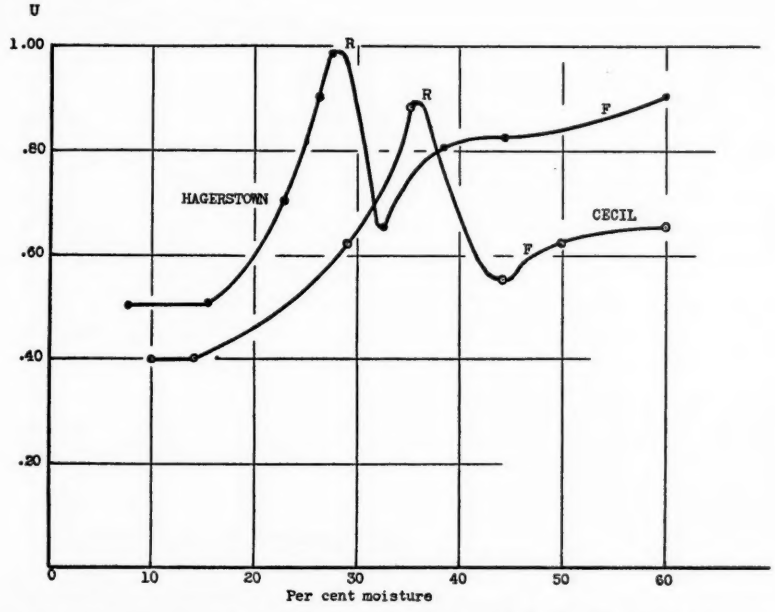

FIG. 3. CHANGE IN THE COEFFICIENT OF STATIC FRICTION WITH INCREASING MOISTURE CONTENT OF THE HAGERSTOWN AND CECIL CLAYS AND THE RELATIONSHIP OF THE CURVES TO THE ATTERBERG CONSTANTS

R and *F* represent rolling and flow limits respectively

The rise in the coefficient of static friction as the soil is wetted above the wilting point is obviously associated with the development of a strong attractive force between the glass and the soil particles through the agency of water. The water films which form around the soil particles at these moisture percentages must be tenacious. The rise here cannot be attributed to increased surface energy resulting from increasing the surface of the air-water interfaces which exist as meniscuses between the wet soil and the watch glass because increasing the contact surface has no influence on the coefficient of static friction. The explanation must be sought for at the soil-water interface.

At the lower moisture contents the film was probably discontinuous and the water molecules were so scattered that only a few contacts were made with the glass surface. It is possible also that much of the moisture held at these percentages was found in small capillaries or even within the crystal lattice and was not connected with the interface. As the soil is wetted, more truly interfacial water appears, more contacts are made, and friction increases to a certain point, after which a drop occurs.

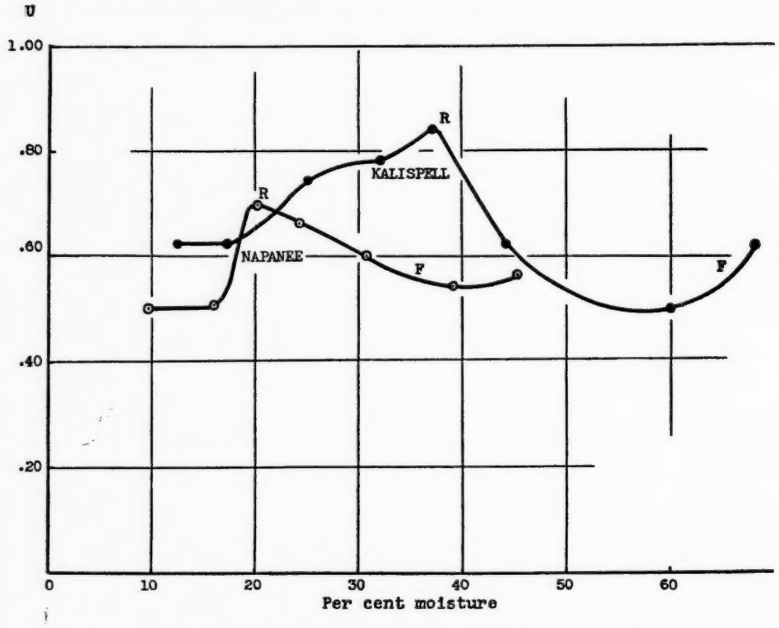

FIG. 4. CHANGE IN THE COEFFICIENT OF STATIC FRICTION WITH INCREASING MOISTURE CONTENT OF THE NAPANEE AND KALISPELL CLAYS AND THE RELATIONSHIP OF THE CURVES TO THE ATTERBERG CONSTANTS

R and *F* represent rolling and flow limits respectively

At this point there must be some abrupt change in the character of the moisture films. One explanation is to be found in the probable complete orientation of water molecules at the solid-liquid interface at low moisture contents, which keeps them in a semi-rigid condition. Because they attach themselves to the glass as well as to the particle surfaces, it is difficult to overcome the adhesive force as long as complete orientation occurs. A progressively more dense layer of such oriented water molecules is probably built up as the soil is wetted more and more. The process may be thought of as the addition of more and more connecting links between the soil particles and the glass surface, each link being more or less rigid and adhering to soil and glass surfaces at

opposite ends. Eventually, at the point when the maximum friction occurs, the molecules of further additions of water are probably no longer oriented and they are free to adjust themselves when a tangential force is applied. The friction is then reduced. When further additions of water are made, increased freedom of molecular adjustment is attained within the water film, and the glass moves progressively more easily as it approaches the moisture content at the flowing limit.

In this connection it is of interest to consider more carefully the discussions of Hardy and Hardy with respect to static friction between glass surfaces. They say:

> The surface film (of fluid or solid) must therefore have a characteristic molecular architecture and the (resulting) condition of minimal potential involves two terms, one relating to the variation of density, the other to the orientation of the fields of force of the molecules. Any polarization of molecules at the surface must introduce a factor in the resistance to (tangential) slip which is absent from any resistance there may be to a displacement along the normal, for the former includes the resistance which the molecules may offer to disturbance of their orientation.
>
> Surfaces whose properties depend upon the interaction of two kinds of states of matter have been called "composite surface."
>
> Two consequences follow—the film resists tangential displacement and therefore has tenacity, and since the potential energy of the molecules composing it is a function of their position, the film is not completely fluid even though it be formed of material which is a fluid when in mass at the same temperature and pressure. Owing to this defect in fluidity composite surfaces are capable of seizing and the static friction of such surfaces is, in our opinion, due to this fact. By seizing is meant the capacity for offering resistance to slip when both faces are at rest.

These investigators found that water in thin films of the order of 1μ was not a lubricant, though in thick films it appeared to be one. The explanation for the rise in static friction in soils, as previously suggested, probably lies in this tendency to seize, and the indications are that up to the point of maximum static friction in soils only oriented water molecules are present, increasing in density per unit area as the moisture content increases. When the friction begins to decrease, the formation of a thicker film in which the molecules are free to move is suggested. If the water molecules in the moisture films were passive, then the increase in the number of contacts between the glass and the soil as the molecular density per unit area of film increased would be ineffective insofar as static friction is concerned, since this would simply amount to an increase in the contact area of inactive surfaces, which is known to bear no influence. The result of a passive condition of the water molecules is shown in the horizontal portion of the friction curves, extending from the air-dry condition to the region of the wilting point.

From these considerations it appears that soil moisture to the lower plastic limit exists as a rigid film of the order of 1μ in thickness. Hardy (6) believes that there may be more than one layer of oriented molecules in a composite surface such as this one. That this may be the case in soils as the rolling limit

is approached seems reasonable because there is probably not enough internal surface to hold the percentage of water present in the soil at this point and have a water layer but one molecule thick. After the point of maximum friction is passed, free moving molecules of water are present, and the forces of fluid surface tension come into play. This is the beginning of the plastic state. At the upper plastic limit the amount of free water is sufficient to cause plastic flow if a liquid-solid phase replaces the solid-liquid phase which characterized the plastic state. Consequently, there are two distinct points of discontinuity indicated in connection with the soil-water system, and the location of these points on the moisture scale corresponds generally with those obtained by Atterberg for his rolling limit and flow limit.

There is some relationship between the magnitude of the coefficient of static friction and the plasticity number in the six clays, but no numerical relationship is suggested, probably because of the wide differences in both colloidal content and chemical composition. The most striking relationship occurs in the case of the glacial clays. The maximum coefficient of friction for the Kalispell clay is 0.84 and that for the Napanee is 0.60; the respective plasticity numbers are 28.9 and 15.7. The Jamaica sample, with a low plasticity number, exhibits only a small rise and fall in friction values, whereas the clays, with high plasticity numbers, exhibit wide variations in friction coefficients at different moisture contents.

DISCUSSION

It is significant that the plastic properties of clays are associated with a certain range in moisture content. The manifestation of plasticity must be intimately connected with the soil-water relationship.

Plastic properties and friction coefficients are no doubt accounted for by the fundamental concept of simple molecular attraction. From a consideration of the work of Hardy and others and orientation of molecules at phase boundaries and from the nature of the changes in static friction at different percentages of soil moisture as shown here the soil moisture relationships appear to be as follows:

In air-dry soil the soil moisture exists in capillaries in the crystal lattice or, at best, in disconnected surface patches with the water molecules oriented and immobile except when heated.

At the wilting point a continuous interfacial film is formed by oriented water molecules, which cover the particle surfaces but are still held strongly by interfacial molecular forces.

At the rolling limit or lower plastic limit the composite film with its oriented water molecules, which are possessed of considerable tenacity, reaches its maximum thickness. This is the point where some freedom of movement among the water molecules is just beginning and a plastic condition appears.

At the upper plastic limit or at the flowing limit a reversal of phases occurs corresponding to a change from a liquid in a solid to a solid in a liquid system.

The answer to the question of the lubricating qualities of water depends on the relationship between the water and the solid interface to which it is at-

tached. When strongly held at the interface through orientation of its molecules, water is not a lubricant but, when its molecules are free to move, it may act like a lubricant to a limited degree.

Varying degrees of plasticity seem to be associated with varying degrees of freedom of movement of water molecules at the solid-liquid interfaces. Surface tension effects at liquid air interfaces within a soil are not enough to account for plasticity or tenacity because in puddled plastic clays such interfaces may not exist. It is likely that the interfacial forces at the solid-liquid phase boundary are of greatest importance in accounting for many of the physical characteristics of clays.

SUMMARY

Static friction measurements having been successfully used in the study of liquid films between glass surfaces, the method was adopted for the study of water films on the surface of clay particles. Six clays were studied over a wide range of moisture, and certain relationships between maximum and minimum points on the curves for static friction and the Atterberg constants were found. The results indicate that the interfacial forces at the soil-water phase boundary are extremely important in the development of many physical properties of soils.

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THE EFFECT OF REPLACEABLE BASES ON THE PHYSICAL PROPERTIES OF SOILS WITH SPECIAL REFERENCE TO THE EFFECT OF REPLACEABLE CALCIUM AND SODIUM ON INDEX OF FRIABILITY[1]

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Received for publication April 24, 1935

Investigations have shown that replaceable calcium and sodium play an important rôle in the reclamation and tillage of agricultural lands in the West. It is generally conceded that physical properties of the soil such as structure, dispersiveness, permeability, cohesive nature, plasticity, water-holding capacity, and friability are affected by the replaceable cations—sodium and calcium. The cation calcium has a desirable effect on the soil, whereas the undesirable effect of the cation sodium can be found in the heavy, cloddy, poorly-drained soils of the West. Most of the high-producing, friable soils of the West and Middlewest have a high percentage of replaceable calcium in the colloidal fraction of the soil. Gedroiz (4) states: "When the soil-absorbing complex is saturated with sodium in a moistened condition it will be a viscous and sticky mass which becomes, on drying, so hard and compact that it is broken into pieces with difficulty and only by the use of high pressures." He is of the opinion, however, that as long as the total replaceable bases in the absorbing complex contain more than 80 per cent calcium, the soil will have maximum friability. The purpose of this experiment was to attempt to measure this change in friability upon soils treated chemically in the laboratory.

Many ways have been suggested for measuring the friability of soils. Workers in the United States Bureau of Chemistry and Soils (2) attempted to measure it by the resistance of the soil to a sharp tool. English workers (5) tried the indirect method of investigating cohesion and plasticity. Middleton (9), in the United States Bureau of Chemistry and Soils, measured the binding power of soils and colloids by means of machines that measured the compressive strengths of briquettes. Stauffer (11) approached the problem from the angle of the tensile strength of the soil. Christensen (3), following the lead of Stauffer, developed a special friability test. He defines the index of friability as the ratio of the unit deformation at the yield point to the work of deformation

[1] Contribution from department of agronomy and soils, Utah Agricultural Experiment Station.

[2] Research assistant, in charge of soils investigations, and research assistant, respectively. Publication authorized by director, April 13, 1935.

at this point. It has the dimensions of the reciprocal of a force per unit area. Christensen's apparatus and method with modifications were used in this work.

The soil used in the present study was a heavy clay soil in poor physical condition collected from the Bell tract near Logan, Utah. The samples used were Nos. 1867 and 1872 used by Harris (6) for his studies on permeability, the former containing small amounts of calcium carbonate (and possibly magnesium carbonate), and the latter, only a trace of inorganic carbonates. No. 2784 (collected directly from the field by the authors) contained small amounts of inorganic carbonates and 0.66 per cent of soluble salts, as determined by the electric bridge method. A chemical analysis of the soluble salts showed chloride and bicarbonate to be the predominating anions and sodium the predominating cation. This sample was used for most of the experimental studies.

METHOD USED IN DETERMINING INDEX OF FRIABILITY AND RELATED PHYSICAL PROPERTIES

Index of friability and related physical properties were determined as follows: 210 gm. of air-dry soil were placed in a large casserole and stirred continuously while water was added slowly by means of a wash bottle. When the soil became wet enough to mold readily and yet was not sticky, it was taken into the hands, and the mixing of the soil and water was continued until the soil paste reached a uniform consistency. The wet soil was then molded into a long cylinder with a diameter slightly less than that of the mold. (A steel mold with a diameter of 2.7 cm. was used for these determinations. The length of the mold was adjusted to 3.37 cm. by means of a piston and threaded cap.) Portions of the soil cylinder were pressed firmly into the mold, smoothed off, removed, and weighed. The soil cylinders thus produced (usually five) were dried for 72 hours in a moist atmosphere and finally at a temperature of 110°C. for 24 hours. The cylinders were cooled in a desiccator, weighed, and the length and diameter of each measured. The compressive strength of each cylinder was determined in the testing machine by obtaining the weight necessary to crush the soil cylinder at the yield point. From data thus obtained, the following physical properties were calculated, using the units indicated: (*a*) shrinkage coefficient (volume of mold taken as standard), (*b*) moisture for molding (M) [dry (110°C.) soil = 0.0 per cent], (*c*) apparent density of dry (ρ) (110°C.) soil, and (*d*) index of friability (I) i.e., reciprocal of compressive strength per unit area $= 1000 \frac{\text{cm.}^2}{\text{kgm.}}$. Physical data shown in figures 1 and 2 and in tables 1, 2, and 3 represent an average for all the soil cylinders molded at one time from each respective 210-gm. sample.

FACTORS INFLUENCING THE INDEX

At the beginning of this work, difficulty was experienced in duplicating results of friability measurements. Variations in density of the soil cylinders

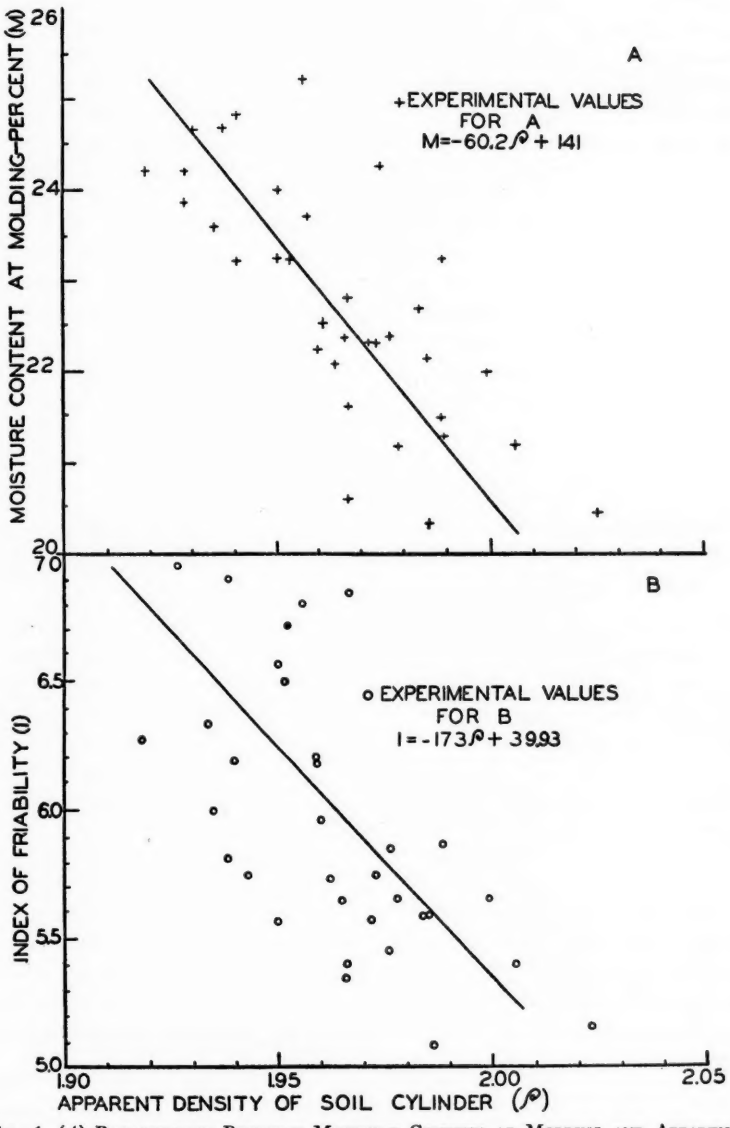

FIG. 1. (*A*) RELATIONSHIP BETWEEN MOISTURE CONTENT AT MOLDING AND APPARENT DENSITY OF SOILS. (*B*) RELATIONSHIP BETWEEN APPARENT DENSITY OF SOILS AND INDEX OF FRIABILITY

was suspected as being the principal cause. This variation was probably due to (*a*) the manner in which the soil is ground and mixed with water; (*b*) the amount of water used in molding; or (*c*) the amount of pressure used in packing the soil into the mold. A quantitative study using Soil No. 2784 was made for factor (*b*), keeping factors (*a*) and (*c*) constant. The statistical relationship of this moisture to apparent density is shown graphically in figure 1-A, and its relationship to index of friability, in figure 1-B. Assuming the relationships to be straight lines within the range of the experiment, the equation for the former is $M = 60.2\rho + 141$, and that for the latter $I = 17.3\rho + 30.93 \pm 0.24$, where M = moisture for molding, I = index of friability, and ρ = apparent density.

There was much less variation in the index of friability when the apparent density was above 1.97 than when below this value (fig. 1-B). This is brought out more forcibly by determination of the standard error of estimate. When the average index of friability for the five soil cylinders is used as the unit,

TABLE 1

Effect of washing soil on index of friability

Soil No. 2784

SUBSTITUTE NO.	BEFORE WASHING			AFTER WASHING		
	Moisture for molding	Apparent density	Index of friability	Moisture for molding	Apparent density	Index of friability
	per cent			*per cent*		
8	22.8	1.967	5.42	22.6	1.971	5.52
12	22.5	1.976	5.48	22.6	1.952	5.77
13	22.2	1.964	5.74	22.6	1.974	5.77
15	21.3	1.978	5.64	22.8	1.956	6.06

this value for the entire density range is ± 0.24. If only cylinders with an average index lower than 1.97 are considered, this value is ± 0.28, whereas, if only those with an index greater than this are considered, the value reduces to ± 0.16. Therefore, in order to obtain the most reliable results for soils similar to Soil No. 2784, it is advisable to produce cylinders with an apparent density above 1.97. This may be done by using just enough water to mold the soil readily, which for this soil was approximately 22 per cent.

Another factor which influences the index is the rate of drying of the soil cylinders. When they were dried too fast, they cracked and the compressive strength of the cylinders was lowered.

All of these factors can be fairly well controlled by carefully following the same method of molding and drying and by using the same amount of water for wetting the soil. These results confirmed the finding of Middleton (9), working in the United States Bureau of Chemistry and Soils with briquettes of soil colloids.

Some samples of soils were washed free of soluble salts in Pasteur-Chamber-

land filters to determine whether their removal from the soil had any effect upon the index of friability. An examination of table 1 shows that washing had little effect. It seems probable that if soils containing large amounts of alkali were washed free from soluble salts, a difference in friability would be noted, as the soluble salts present in the soil solution may have a flocculating effect on the colloidal material or they may affect the replaceable base equilibrium in the soil.

CHEMICAL TREATMENT OF SOILS

According to the present-day theory, replaceable base reactions take place primarily in the colloidal fraction of the soil. The bases exist as portions of true chemical compounds and can be removed from the soil only when another base or hydrogen takes their place. Several methods have been used for replacing bases in soils. The one used in this work was as follows:

Two hundred and ten grams of soil were given a substitute number, divided into three 70-gm. portions, and each placed in a large Erlenmeyer flask, with 250 cc. of a normal chloride solution. The cation associated with the chloride in the treating solution was either a single base, such as sodium or calcium, or a mixture of two bases. The flasks were shaken several times a day, and the suspension was allowed to settle overnight. The following morning the clear solution was syphoned off, and 250 cc. more solution was added. This was repeated several times, usually for 8 or 10 days.

After the required number of applications, the soil was washed five times through a Pasteur-Chamberland filter in order to remove the soluble salts. Before each washing, the entire 70 gm. of soil was shaken with distilled water in a mechanical shaker. After washing, the three 70-gm. portions of soil were mixed and allowed to dry. The water required to remove the soil from the filter was evaporated at about 40°C., and the bulk of the soil was dried at room temperature. After drying, the soil was ground to pass a 1-mm. sieve and then thoroughly mixed. This entire procedure is spoken of as a "treatment."

ANALYSIS FOR REPLACEABLE BASES[3]

The method used to remove the replaceable bases from the soil for analysis was similar to the first part of the treatment as described. A 15-gm. portion of soil was treated with six applications of an aqueous solution of 0.1 *N* ammonium acetate, and a separate 15-gm. portion was treated with seven applications of 0.1 *N* potassium chloride in 50 per cent alcohol. All treatments were run in duplicate. The solutions syphoned from the six ammonium acetate applications were made up to a given volume, and aliquot portions were analyzed for sodium and potassium, respectively. Sodium was determined

[3] The method used to determine calcium and magnesium in calcareous soils was one developed by Joel E. Fletcher in this laboratory (unpublished).

by the zinc uranyl acetate method, and potassium, by the perchloric acid method.

Most of the soils studied contained some calcium carbonate (and possibly magnesium carbonate); therefore, in order to make the determinations of replaceable calcium and magnesium more reliable, it was necessary to reduce the solubility of their carbonates to a minimum and make a correction for the solubility factor. The method used was based on the assumption that the solubility remained constant throughout the treatment.

Solutions syphoned from the first five applications of 0.1 *N* potassium chloride solution were mixed and made up to a given volume, and an aliquot portion was analyzed for calcium and magnesium. Solutions from the sixth and seventh applications were mixed and analyzed for soluble calcium and magnesium. Replaceable calcium and magnesium were calculated by subtracting 5/2 of the respective amounts found in the latter determination from the amounts found in the former.

GENERAL EXPERIMENTAL PROCEDURE

After the method for determining the index of friability had been well standardized, the following methods of procedure were used to determine the relationship between replaceable bases and various physical properties. The soil was ground to pass through a 1-mm. sieve before each determination.

The index of friability and related physical properties were determined for each soil sample, as described, before any treatments were made and again after the soil had been given the chemical treatments indicated in the following. The data are recorded in tables 2 and 3. Only the average value for the untreated soil is given.

Soil samples were treated with eight or ten applications of the respective single chlorides, sodium, calcium, and magnesium, and with various mixtures of sodium and calcium chlorides, as indicated in table 2.

Samples from Soil No. 2784, previously treated with sodium chloride, were retreated with one or more applications of calcium chloride, as indicated in table 3.

Friability measurements similar to those described, except that the drying process was interrupted at various stages and the cylinders were broken while they still contained moisture, were made for respective sodium-and calcium-treated samples (Soil No. 2784) in order to determine the relationship between the index of friability and the moisture content at breaking. Some of the samples were reground and remolded several times in order to obtain a variation in the moisture content at breaking (dry 110°C. soil = 0.0 per cent), which was determined by drying portions of the broken cylinders at 110°C. The relationship of moisture content at breaking to index of friability is shown graphically in figure 2.

Attempts were made to measure the physical properties for a bentonite (Soil No. 2788), but difficulty was encountered in drying the molded samples without their cracking. Both untreated and chemically-treated samples were used.

Replaceable bases were determined as previously described, for soils treated chemically. Replaceable sodium was determined for an untreated sample by subtracting the soluble sodium from the total amount removed during treatment with ammonium acetate. No attempt was made to determine replaceable calcium in the untreated soil because the solubility of calcium carbonate would be much lower at the beginning of the treatment when large amounts of soluble bicarbonate were present than later in the treatment when a portion of this anion had been removed. Data obtained are recorded in table 4.

DISCUSSION OF RESULTS[4]

The data presented herein, as well as observations made while obtaining these data, show that some physical properties of soils are altered materially by base exchange while others apparently are not.

During the washing process the maximum concentration of sodium chloride which permitted the dispersion of the sodium soil was higher than the maximum concentration of calcium chloride which permitted the dispersion of the calcium soil. It required about twice as long to wash samples treated with sodium as it did to wash calcium-treated samples, because of the failure of the highly

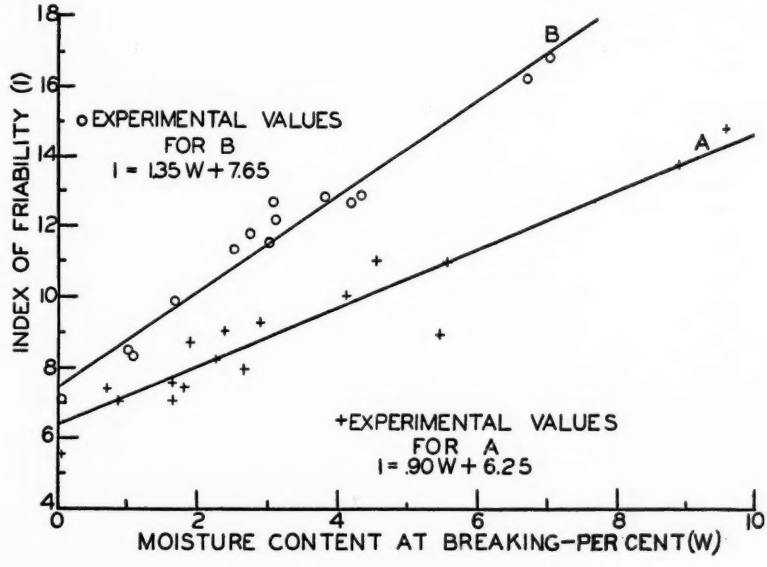

FIG. 2. RELATIONSHIP BETWEEN THE MOISTURE CONTENT AT BREAKING AND INDEX OF FRIABILITY FOR CHEMICALLY-TREATED SOILS. (*A*) SODIUM-TREATED SOILS. (*B*) CALCIUM-TREATED SOILS

dispersed sodium soil to settle below the filter as well as of low permeability to water. In all cases the first two washings from the sodium-treated samples were dark-colored. The dark color was probably due to some of the humus dispersoids going into colloidal solution, since the sodium humus dispersoids are more readily dispersed than the corresponding calcium dispersoids. Another difference between sodium- and calcium-treated soils was the greater tendency for the sodium-treated soil to crack during the process of drying. In the case of the bentonite used, the tendency to crack was so great that all

[4] A discussion of chemical equilibrium relationships of the replaceable bases will be included in a forthcoming publication by J. Darrel Peterson and D. S. Jennings.

samples were affected. Cylinders produced from sodium-treated bentonite, however, were more warped and distorted than those produced from calcium-treated bentonite.

TABLE 2

Physical properties of soils with one chemical treatment

(8 or 10 applications)

NO.		CHEMICAL APPLIED	MOISTURE FOR MOLDING	SHRINKAGE COEFFICIENT	INDEX OF FRIABILITY	APPARENT DENSITY
Laboratory	Substitute					
			per cent			
2784	Average	Untreated	22.6	17.61	5.79	1.973
2784	Av. for 9 samples	1 *N* NaCl	22.8	18.44	5.50	1.995
2784	Av. for 5 samples	1 *N* $CaCl_2$	23.6	19.38	7.39	1.984
2784	15	0.25 *N* NaCl + 0.75 *N* $CaCl_2$	22.2	18.46	8.25	1.974
2784	16	0.25 *N* NaCl + 0.75 *N* $CaCl_2$	21.6	18.02	7.20	2.014
2784	6	0.5 *N* NaCl + 0.5 *N* $CaCl_2$	21.2	17.97	7.81	1.999
2784	13	0.5 *N* NaCl + 0.5 *N* $CaCl_2$	21.6	16.52	7.58	1.989
2784	12	0.75 *N* NaCl + 0.25 *N* $CaCl_2$	22.1	17.92	7.96	1.986
2784	18	0.75 *N* NaCl + 0.25 *N* $CaCl_2$	21.4	17.66	7.30	1.990
1867	1	1 *N* NaCl	22.0	.....	7.50	.....
1867	2	1 *N* KCl	24.0	.....	14.50	.....
1867	3	1 *N* $CaCl_2$	25.0	.....	10.10	.....
1872	1	1 *N* NaCl	26.0	.....	7.64	.....
1872	2	1 *N* KCl	24.3	.....	11.20	.....
1872	3	1 *N* $CaCl_2$	28.0	.....	10.90	.....
1872	4	1 *N* $MgCl_2$	27.0	.....	10.90	.....

TABLE 3

Physical properties of sodium-treated soils treated subsequently with calcium

Soil No. 2784

SUBSTITUTE NO.	NUMBER APPLICATIONS OF $CaCl_2$	MOISTURE FOR MOLDING	SHRINKAGE COEFFICIENT	INDEX OF FRIABILITY	APPARENT DENSITY
		per cent			
22	1	24.3	19.53	6.43	1.985
23	1	24.5	19.68	6.43	1.981
21	3	25.0	20.51	6.85	1.973
24	3	24.0	19.17	6.76	1.978
5	10	22.5	20.51	7.20	1.985

Since physical properties measured are interdependent, it is necessary to consider certain conditions or values constant, within experimental limits, when discussing the influence of replaceable bases upon them. The apparent density is the value considered constant throughout the following discussion.

Keen (7) shows that for a given soil there is a definite relationship between shrinkage coefficient and moisture content at time of molding. Puri (10) was unable to find any difference in the shrinkage coefficient (moisture content at time of molding being kept constant) when comparing sodium-treated soils with calcium-treated soils. The data presented in table 2 are, within experimental error, in agreement with this work. The data show that the relation-

TABLE 4

Replaceable bases in chemically-treated soils

(M.e. per 100 gm. of soil)

NO.		CHEMICAL APPLIED	REPLACEABLE BASES PRESENT	
Laboratory	Substitute		Ca	Na, K, or Mg
				Na
2784	AF	Untreated	.....	16.86
2784	7	1 *N* NaCl	10.60	6.90
2784	14	1 *N* NaCl	10.10	6.12
2784	25	1 *N* NaCl	10.50	5.56
2784	10	1 *N* $CaCl_2$	17.18	0.98
2784	11	1 *N* $CaCl_2$	17.70	0.47
2784	15	0.25 *N* NaCl + 0.75 *N* $CaCl_2$	17.34	1.20
2784	6	0.5 *N* NaCl + 0.5 *N* $CaCl_2$	16.47	1.51
2784	13	0.5 *N* NaCl + 0.5 *N* $CaCl_2$	15.15	2.49
2784	12	0.75 *N* NaCl + 0.25 *N* $CaCl_2$	16.26	1.42
2784	22	1st, 1 *N* NaCl −2d, 1 application $CaCl_2$	17.85	0.30
2784	23	1st, 1 *N* NaCl −2d, 1 application $CaCl_2$	17.85	0.13
2784	21	1st, 1 *N* NaCl −2d, 3 application $CaCl_2$	17.10	0.18
2784	24	1st, 1 *N* NaCl −2d, 3 application $CaCl_2$	16.48	0.16
2784	5	1st, 1 *N* NaCl −2d, 10 application $CaCl_2$	18.33	0.43
1867	1	1 *N* NaCl	12.93	3.68
1867	3	1 *N* $CaCl_2$	18.43	0.03
1872	1	1 *N* NaCl	3.72	12.19
1872	3	1 *N* $CaCl_2$	15.02	0.02
				K
1867	2	1 *N* KCl	7.08	11.13
1872	2	1 *N* KCl	2.71	14.11
				Mg
1872	4	1 *N* $MgCl_2$	0.72	17.73

ship between the moisture content at molding and the shrinkage coefficient is unaltered by base exchange. It may be that more refined measurements would show a difference.

An examination of table 4 shows that replaceable sodium was lower in sodium-treated Soils Nos. 1867 and 2784 containing calcium carbonate than in Soil No. 1872 containing practically no calcium carbonate, that samples treated with a mixture of sodium and calcium contained mainly replaceable

calcium, and that sodium-treated samples treated subsequently with one or more applications of calcium chloride contained practically no replaceable sodium. Kerr (8) and Vanselow (12) indicate that if a soil is treated with a mixture of salts, the resulting soil will contain a mixture of replaceable bases. The failure in this case to produce a soil containing both replaceable sodium and calcium and to saturate the soil with sodium may be accounted for by the presence of calcium carbonate in the soil. Samples treated entirely or partially with sodium chloride probably contained more replaceable sodium before the soluble salts were removed than after they had been eliminated. The calcium bicarbonate dissolved by the water from the soil during the washing process probably acted as a replacing agent and removed a portion or all of the replaceable sodium. In case of the sodium-treated samples treated again with one or three applications of calcium chloride, the replacement probably took place in two steps. A portion was replaced with the calcium chloride and the remainder with calcium bicarbonate.

The index of friability is dependent upon the chemical treatment of the soils (table 2). The soils treated with sodium had a lower index than soils treated with calcium. In case of Soil No. 2784, the average index of friability for the sodium samples was 5.50 and that for the calcium samples was 7.39, an increase of 1.89, or 34 per cent. Although this difference is not great, it shows that a sodium soil will be more difficult to plow or to cultivate than a calcium soil. The few determinations made for magnesium- and potassium-treated soils indicate an effect similar to calcium.

Certain properties of soils apparently depend upon previous treatment of the soil as well as upon the replaceable bases present. Volk (13) reports that potassium in potassium-treated soils can be changed from a replaceable to a non-replaceable form by wetting and drying the soil several times. Puri (10) found that if the sodium from sodium-treated soils were replaced by some other cation and the soil never allowed to dry, the latter would remain dispersed as though it were still sodium-saturated, but that if it were allowed to dry it would acquire the characteristics normally produced by the cation substituted. Burgess and Breazeale (1) apparently failed to recognize this fact when they reported that even small amounts of sodium would cause the soil to be dispersed. Harris (6) worked with soils in which the difference in replaceable base content was produced naturally in the fields where the soil had been subject to wetting and drying several times; consequently, he was able to find a relationship between percentage of replaceable sodium and permeability to water. The concentration of the treating solution seems to determine to some extent the physical properties of the soil after treatment. In this laboratory a sodium-treated bentonite treated again with 0.1 *N* ammonium acetate remained dispersed even after the replaceable sodium was all removed, but when solid ammonium acetate was added to the sodium-treated bentonite first and water added in small portions it remained flocculated through out the entire treatment.

The theory of influence by previous treatment probably will explain the fact that the index of friability corresponds more closely to the treatment of the soil than to the replaceable bases present in the soil after treatment (tables 2, 3, and 4). The index found is probably dependent upon the replaceable sodium in the soil before washing and not upon that in the soil after washing. The removal of the replaceable sodium by dilute calcium bicarbonate while the soil is dispersed leaves the physical properties of the soil comparatively unchanged, but the removal of replaceable sodium with normal calcium chloride while the soil is flocculated produces a change in physical properties. This will account for the fact that the variation in index of friability for sodium- and calcium-treated soils for Soils Nos. 1867 and 2784 is about the same as that for Soil No. 1872 from which the replaceable sodium was not removed by calcium bicarbonate. It will also explain why certain sodium-treated samples (Soil No. 2784) treated subsequently with calcium chloride possessed an index of friability in between that sodium- and calcium-treated samples. The amount of sodium removed by calcium chloride will depend upon the number of applications; therefore, the samples again treated with the smallest number of applications should have the lowest index of friability. An examination of tables 2, 3, and 4 shows this to be the case. Substitute Nos. 22 and 23, again treated with one application of calcium chloride, had a lower index of friability than Substitute Nos. 21 and 24 again treated with three applications, whereas Substitute No. 5, again treated with ten applications, had an index similar to the calcium-treated soils. This theory fails to show, however, why the samples treated with a mixture of sodium and calcium should have the highest index of friability. This, however, may be due to errors made in making measurements of index of friability.

Data obtained (fig. 2) indicate that the difference between the index of friability for calcium-treated and sodium-treated samples (Soil No. 2784) is greater when the soil contains some moisture than when the soil is dry. The index increases with increasing moisture content for both types of soil, but the increase is greater for calcium soil. Both relationships are apparently straight lines. The equation for the sodium soil was $I = .90\ W + 6.25$ and that for the calcium soil was $I = 1.35\ W + .65$, where I equals index of friability and W equals moisture content at breaking. It was impossible to obtain data for samples with more than 10 per cent moisture because, instead of breaking under pressure, the soil cylinders had a tendency to flatten.

SUMMARY

A study was made of the influence of replaceable bases on various physical properties of soils, with special reference to the influence of replaceable calcium and sodium on the index of friability.

Modifications are reported in Christensen's method for determining the friability of soils. The determinations reported in this study indicate that treating the soil with sodium lowers the index of friability, thus producing a soil inferior in physical condition to calcium-treated soils.

The difference between the index of friability of a sodium-treated and a calcium-treated soil is greater for the wet than for the dry soil.

It was found that the index of friability of soils corresponds more closely to the chemical treatment than to the replaceable bases present after treatment. The theory advanced to explain this fact assumes that the physical properties of sodium soil are changed if the replaceable sodium is removed by high salt concentration, such as a normal solution of calcium chloride, whereas the physical properties are comparatively unchanged if the sodium is removed by dilute solutions, such as calcium bicarbonate formed from calcium carbonate in the soil.

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STUDIES ON THE SURFACE BEHAVIOR OF BENTONITES AND CLAYS[1]

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Received for publication June 22, 1935

Application of electrostatics has met with considerable success in the explanation of the behavior of systems the components of which possess marked electrical character. The interaction of clays with water and aqueous solutions of electrolytes where the acting agents are charged surfaces, ions, and dipoles should, therefore, be mainly a function of their electrical character. The main difficulty in the application of electrostatics to the explanation of the actual behavior of clays toward water and ions lies in the indeterminacy of the structure of the electric field at the surface of the colloidal particle. Obviously, the best application that can be made of the theory is to calculate the behavior of clay-water systems on the basis of logical assumptions and to accept as facts those assumptions which lead to the best mathematical description of the observed phenomena.

Duclaux (3) has calculated the distribution of ions around a spherical particle of opposite charge. His equation, the derivation of which will be brought out later in this paper, shows that the thickness of the ionic atmosphere around a colloid particle is of the same order of magnitude as the particle itself. Consequently, the Duclaux formula can be expected to hold only when the colloidal particle possesses a spherical shape and uniformly distributed charge. In the case of soil colloids where there is no *a priori* reason why they should have any particular form, and where usually both cation and anion exchanges are found, this equation cannot be expected to possess general applicability.

The physico-chemical behavior of the surface of a colloidal particle is a function of both the geometrical and electrical properties of this surface. From a geometrical viewpoint the surface may be of the convex, plane, or concave type. Electrically, it may represent a sparse to dense system of point charges of either the same or of opposite sign. In the following, equations are given for the ideal convex surface (sphere) as well as for the plane surface type, developed under the assumption of a uniform and, for the plane type, relatively dense surface charge. The influence of variations in the electrical character will be treated later.

[1] Published with the approval of the department of soils, University of Missouri, Columbia, Missouri, and of the Missouri State Highway Department, Jefferson City, Missouri.

[2] Research chemist, Missouri State Highway Department.

The equation for the distribution of ions around a charged sphere has been developed by Duclaux as follows:

If
e = the elementary electric charge
P = the number of the swarm ions
p = the charge of the swarm ions
N = the Avogadro number
c = the number of ions per unit volume
r = the distance from the center of the granule
dr = an increment of distance
ds = an element of surface
K = the dielectric constant of the liquid medium
R = the gas constant
T = the absolute temperature

then the electrostatic attraction of the granule on the ions contained in the volume element $ds \cdot dr$ is

$$E = \frac{Pp^2e^2cdsdr}{Kr^2}$$

and the resultant of the osmotic pressures on the two sides of the volume section $ds \cdot dr$ is

$$O = \frac{RT}{N} \cdot \frac{dc}{dr} \cdot ds \cdot dr$$

therefore, in the state of equilibrium

$$\frac{Pp^2e^2cdsdr}{Kr^2} = \frac{RT}{N} \frac{dc}{dr} \cdot d\,s \cdot dr$$

which on integration gives

$$c = Ae^{*\,\frac{Pp^2e^2N}{KRT}\frac{1}{r}}$$

A plane surface structure is defined as one in which charge points of the same sign are densely and uniformly spread over a plane surface. In this case the Faraday lines will run parallel in a right angle from the surface and will end in the oppositely charged ions. Figure 1 shows pictures for the convex and for the plane surface field.

The equation for the electrical attraction in the case of the plane field structure is then

$$E = \frac{Pp^2e^2cdsdr}{Kr}.$$

* e, basis of natural logarithms.

and for the equilibrium of osmotic and electrical forces,

$$\frac{Pp^2e^2cdsdr}{Kr} = \frac{RT}{N}\frac{dc}{dr} \cdot ds \cdot dr$$

$$\frac{dc}{c} = \frac{NPp^2e^2}{KRT}\frac{dr}{r}$$

or if

$$\frac{NPp^2e^2}{KRT} \text{ is kept constant } = k$$

$$ln\, c = K\, ln\, r + A$$
$$c = Br^k$$

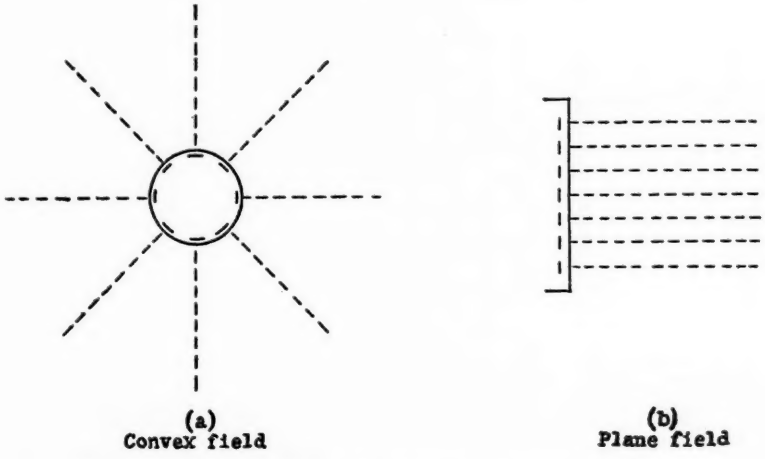

FIG. 1. ELECTRICAL SURFACE STRUCTURE OF COLLOIDAL PARTICLE

Calculations on concentrations of mono, bi, and trivalent ions at different distances from the surface of a spherical granule of 2 mμ radius and with 12 negative charges are given in table 1. The physical magnitudes used in the calculations are:

$$e = 4.8 \cdot 10^{-10} \text{ electrostatic units}$$
$$N = 6 \cdot 10^{23}$$
$$K = 80$$
$$RT = 2.38 \cdot 10^{10} \text{ erg}$$

After insertion of the numerical values in the equilibrium equation for the plane shaped particle it becomes apparent that k is approaching zero sufficiently to render $r^k = 1$, and $c = B$.

An analysis of the equations for the convex and for the plane field shows

that in the first case the ionic concentration is very high close to the surface and falls off rapidly with increasing distance. This decrease becomes more rapid with increasing charge of the ions. In the case of the plane surface the concentration stays practically constant with increasing distance from the surface. It should be kept in mind, however, that these data are calculated

TABLE 1

Distribution of ions around a spherical colloidal particle (3)

DISTANCE FROM SURFACE	CONCENTRATIONS		
	C_1 Monovalent ions	C_2 Divalent ions	C_3 Trivalent ions
mμ			
0	63 A_1	40 A_2	25 A_3
1	16 A_1	2.5 A_2	0.40 A_3
2	8 A_1	0.63 A_2	0.05 A_3
4	4 A_1	0.32 A_2	0.003 A_3
8	2.3 A_1	0.05 A_2	0.001 A_3
30	1.2 A_1	0.02 A_2	0.0002 A_3

A_1, A_2, and A_3 are constants.

TABLE 2

Physico-chemical properties of some colloidal clays

PROPERTY	TYPE OF H-COLLOID					
	Bentonite	Lufkin clay	Wabash clay	Putnam clay	Susquehanna clay	Cecil clay
SiO_2–R_2O_3 ratio	5.0	3.8	3.2	3.2	2.3	1.3
Exchanged capacity, m.e./gm.	0.95	0.82	0.78	0.65	0.47	0.13
Swelling,* cc./gm.	2.20	1.18	0.94	0.81	0.57	0.05
Heat of wetting, cal./gm.	(16.0)	15.0	13.9	13.8	11.7	5.9
Hygroscopicity (30 per cent H_2SO_4), per cent by weight	21.5	20.1	.....	18.1	15.5	6.1
Swelling, cc. / Heat of wetting, cal./gm.	(0.14)	0.08	0.07	0.06	0.05	0.01
Swelling, cc. / Exchange capacity, cal./gm.	2.44	1.44	1.20	1.24	1.21	0.41
Heat of wetting / Exchange capacity	(16.8)	18.3	17.8	21.2	24.9	46.4

* Measured by the Winterkorn-Baver method.

for an ideal case. Actually, an ideal plane field will never be encountered on the surface of the colloidal granules. Moreover, if it would exist close to the surface it would be dispersed with increasing distance, because of the limited size of the plane as well as the fact that the electrical force lines end in the swarm ions.

It is obvious that, if the active volume of the colloidal particle consists of the volume of the granule and of the denser part of the ionic atmosphere, a larger active volume in the case of a plane field structure will be found than in the case of a spherical particle shape. Since in the aforementioned derivations the repulsive action of the ions composing the atmosphere has been neglected, the values for the active volumes of the particles calculated by means of these equations represent minimum values. It should be further kept in mind that the dielectric constant of water approaches 3 in very strong

TABLE 3

Data on swelling and dispersity of clays and bentonite

TYPE OF CLAY	SiO_2–R_2O_3	SWELLING, CC./GM.					
		H	Li	Na	K	Ca	Ba
Bentonite	5.0	2.22	10.8	11.1	8.6	2.5	2.5
Putnam	3.2	0.81	5.0	4.0	0.5	0.91	0.85
Wabash	3.2	0.94	3.1	3.7	0.55	0.79	0.74
Iredell	1.8	0.23	0.42	0.6	0.02	0.30	0.36
Dispersity < 100 mμ							
Bentonite	5.0	34.0	37.8	35.2	35.7	31.2	31.9

TABLE 4

Symmetry values of clays and bentonites

TYPE OF CLAY	NATURE OF CATION					
	Li	Na	K	Ca	Ba	H
NH_4·Putnam	29.9	35.3	51.3	63.6	71.6	84.9
H·Putnam	6.6	6.2	14.5	26.9	23.8	....
H·Bentonite	18.0	14.6	18.4	....	....	....
Release						
NH_4Cl + Putman clay	57.0	58.9	42.0	29.3	....	6.9
NH_4Cl + Bentonite	46.5	49.6	43.7	....	....	14.5

electric fields. Another important point which has been neglected is the hydration of the ions, or, more generally, the polarization effects in the system.

Beside the rôle that they play in the hydration of the ions and of electrically charged surfaces, polarization effects appear also to be responsible for the anomalies in the exchange of bivalent ions. For example, with monovalent ions easy adsorption corresponds with difficult release; on the other hand, with divalent ions easy adsorption and easy release go parallel. For a complete electrostatic analysis of this problem energy calculations would have to be made for a system for the cases: (*a*) that the cation is entirely hydrated and is found as close to the negative charge as its hydration hull permits; (*b*) that

the cation is completely dehydrated and that besides the coulombic attraction of the ion and the oppositely charged surface, attraction due to polarization plays a significant rôle; and (*c*) that the cation is dehydrated only at the side adjacent to the negative charge, and that the energies of the partial hydration, of the ionic attraction, and of the polarization effects come into play. The data needed for quantitative information on the probability of these three conditions represent relatively small differences of rather large magnitudes; unfortunately they cannot yet be determined or calculated accurately enough to be used as a convincing argument. Nevertheless, a qualitative explanation is rather easily conceived. If we assume, as seems logical, that the negatively charged oxygen at the colloidal surface which is held by part of the positive charges of a silica ion below the surface is in a similar electric condition as the oxygen in a hydroxyl ion, then the magnitude of the polarization effect of the bibalent ion on the surface oxygen should be similar to that on the hydroxyl ion. Consequently, the ease of release of such a cation from a colloidal surface should run parallel to the ease of dissociation and, therefore, to the solubility of its hydroxide in water. This has been shown experimentally (5).

With the exception of the case where the polarization of the surface of a colloidal granule by a cation would result in a greater decrease in free energy than is connected with the hydration of the ion, this ion can approach the surface only as closely as its hydration permits. In the case of spherical granules, where the ionic density is very large close to the surface, it should be expected that the increase in apparent volume in a liquid is largely governed by the solvatation of the ions, and that swelling is, therefore, closely connected with the heat of wetting (4).

Because of the greater proximity of the majority of the swarm ions to the surface of a spherical particle, the individual properties of the ions, such as size, charge, polarizability, and polarizing power, should exert a more pronounced influence on the base exchange properties of such a colloid than on the properties of a colloid with plane surface structure.

Plasticity studies and microscopic examinations of oriented aggregation of clays indicate that most of the common clays possess a geometrical plane structure. On the other hand, studies of their colloidal properties show that they possess cation and anion exchange capacities, the latter increasing with decreasing SiO_2–R_2O_3 ratio of the colloid. It appears worthwhile, therefore, to discuss generally in which direction a heterogeneously charged system will change the properties as derived from the assumption of a plane surface with uniform charge.

If the surface represents a system of positive and negative points, and if the ionic atmosphere consists of negative and positive ions, then the decrease of the strength of the surface field will be a function of a power of the distance higher than the first; thus, the character of the ion atmosphere will approach that of the swarm around a spherical granule. This tendency to greater compactness of the ionic atmosphere will be fostered by a decrease in the repulsion

of ions of the same kind of charge due to the presence of those with opposite sign. On the other hand, positive surface charges which are situated close to a negative charge will counteract the attraction of a swarm cation by this charge (*et vice versa*). This will effect a better exchangeability, especially in the case of those ions which are generally held very strongly at the surface (6).

Table 2 shows experimental data on the properties of different clays (2). Some interesting relationships are brought out. In the light of the theory developed in the foregoing it appears especially important that, although the ratio of heat of wetting to exchange capacity for bentonite, Lufkin, and Wabash clay indicates that the H ions are in the same state of hydration, the ratio of swelling to exchange capacity shows that in the case of bentonite the ion atmosphere is more diffuse. Bentonite, therefore, appears to be representative of clays with the plane type of surface structure. Another interesting fact is the increase of the ratio of heat of wetting to cation exchange capacity and the decrease of the ratio of swelling to heat of wetting and of swelling to cation exchange capacity with decreasing SiO_2–R_2O_3 ratio. It is generally known that the anion exchange capacity of clays increases with decreasing SiO_2–R_2O_3 ratio, i.e., with the decrease of this ratio the number of positive charges in the surface increases. The foregoing data as well as those of other investigators (4) suggest that, because of their connection with relatively large silica-oxide complexes, the negative charges are situated too far inside the surface to bind water with any appreciable thermal effect. Positive charges, on the other hand, originating from iron and alumina in the surface seem, according to these data, to be able to orient and eventually polarize water molecules. This view is further strengthened by the observations of Baver and Horner (1) that with decreasing cation exchange capacity and with decreasing SiO_2–R_2O_3 ratio soil colloids absorb less water at low but retain more at high temperatures.

After the identification of bentonite as representative of the clays with plane type of surface structure and of the common clays as approaching in their behavior that of the convex type of surface, it should be expected that the individual characteristics of the swarm ions affect the properties of clays more than they affect those of bentonites. This view is confirmed by the data in tables 3 and 4 (2).

With bentonite the swelling is of the same order of magnitude whether the exchange complex be saturated with Li, Na, or K; however, with clays the swelling in the case of K saturation is much smaller than with the Li and Na saturation. The similarity of the effect of Li, K, and Na ions on bentonite is also shown by the dispersity data. The same relationship holds true in the case of the symmetry values.

On the assumption of a plane surface structure for bentonite, its thixotropic character is also readily explained. Since the preceding rather elementary application of electrostatics resulted in the explanation of the general difference in the behavior of clays and bentonites, it is felt that further consequent use of electrostatics will help in elucidating still other phases of the surface behavior of these substances.

SUMMARY

An attempt has been made to explain the general difference in the behavior of bentonites and clays on the basis of the electrical properties of their surfaces. Experimental data are given in support of the theoretical conclusions.

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NOTES ON ESTIMATING AVAILABLE PHOSPHORUS BY EXTRACTING SOILS WITH A POTASSIUM CARBONATE SOLUTION

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Received for publication June 24, 1935

Das in 1926 (1) and again in 1930 (2) described a method of estimating available phosphorus in soils by extracting with a dilute potassium carbonate solution. His results showed that the method was equally applicable to all types of soil and that it had the advantage over acid extraction methods in that it could be used in alkaline calcareous soils where acid extraction methods were not reliable. Hockensmith et al. (3) in 1932 found that a modification of the Das method, consisting of a hot rather than a cold extraction, distinguished between phosphate deficient and sufficient soils in Colorado in a high percentage of cases.

Since there is a large area of alkaline calcareous soils in the western United States where acid extraction methods are not reliable and since there is a great need of a reliable method in this area, the authors believe that the use of an alkaline extractant deserves further study by soil investigators. It is with the hope of stimulating further investigation that the following procedure is submitted. The procedure as originally published by Hockensmith et al. had the disadvantage that the color faded quickly and was often cloudy so that accurate determination of the phosphorus was difficult. The revised procedure gives a color which is usually stable for several hours and is seldom cloudy. The method of determining the phosphate in the potassium carbonate extract is also applicable to other phosphate solutions.

PROCEDURE

Weigh out a 2-gm. sample of soil, which has been passed through a 1-mm. sieve, and place in a 250-cc. flask. Add 150 cc. of a 1 per cent solution of phosphorus-free potassium carbonate and place on a previously heated hot plate. The temperature should be regulated so that the solution simmers for about 45 minutes. In 60 minutes,[1] remove the flask and allow it to cool. After settling for 12 to 24 hours,[2] transfer 10 cc. of the supernatant liquid to a 100-cc. Erlenmeyer flask. Add 1 cc. of bromine water. Heat to boiling,[3] and add

[1] It was found in the laboratory that digestion for less than an hour decreases the phosphorus content. However, prolonged digestion affects the phosphorus but little.

[2] The cooled sample may be centrifuged to obtain a clear solution if speed is essential.

[3] This may be accomplished conveniently on an electric hot plate. The solution should not be allowed to evaporate to dryness.

0.4 cc. of 5 *N* HCl, and 0.5 cc. of 10 per cent sodium sulfite. The extract should be clear at this point. Remove and cool. Neutralize (1 drop in excess) with 0.5 *N* NaOH, using 1 drop of 0.25 per cent alcoholic phenolphthalein as the indicator. If the end point is over-run, titrate back with 0.5 *N* sulfuric acid. Make up to 15 cc. with distilled water and shake.

To the slightly pink solution, add 1 cc. of the molybdic oxide reagent from a burette. Shake, add exactly 0.2 cc. of stannous chloride reagent, and mix well. After 5–10 minutes,[4] place 10 cc. of the solution in a square test tube and compare the color with the standard phosphate solution, using any good color comparator.

Solutions

Potassium carbonate—1 per cent by weight K_2CO_3. Of this solution 150 cc. should be drawn off and tested for freedom from phosphorus by the foregoing method.

Bromine water—saturated.

Hydrochloric acid—approximately 5 *N*.

Sodium sulfite—10 per cent—C.P. grade. Make up fresh about every 2 weeks.

Sodium hydroxide—approximately 0.5 *N* NaOH.

Sulfuric acid—approximately 0.5 *N* H_2SO_4.

Molybdic oxide reagent (4)—add 6.02 gm. C.P. anhydrous MoO_3 to 120 cc. of concentrated H_2SO_4 (sp. gr. 1.84: 94 per cent). Heat with stirring until dissolved. Cool and make up to 800 cc. with distilled water.

Stannous chloride—stock solution. Dissolve 25.5 gm. $SnCl_2 \cdot 2H_2O$ in 125 cc. of HCl (sp. gr. 1.18: 35–7 per cent) and make up to exactly 1 liter. Keep under white mineral oil in a dark bottle. If kept in a cool place, this solution will keep indefinitely.

Work solution. Quantitatively dilute 50 cc. of the stock solution to 250 cc. (dil. 1–5) with pure distilled water. This solution must be renewed every 2 or 3 days, or when it turns yellow.

When the foregoing procedure is used, 37 parts phosphorus extracted per million parts soil are equivalent to 55 p.p.m., by the procedure of Hockensmith et al. (3). This has been shown to be approximately the dividing line between deficient and sufficient soils for the soils studied.

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[4] The color will be very nearly constant after standing for 5 minutes. The intensity will not change enough to be detected for at least 15–20 minutes. However, it is better to make the comparison after 5–10 minutes.

SHOT SOILS OF WESTERN WASHINGTON[1]

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Received for publication June 25, 1935

Most of the upland soil types of western Washington, a humid region west of the Cascade mountain range, are characterized by the presence of a considerable number of hard, rounded pellets distributed throughout the developed portion of the soil profile. These pellets vary from the dimensions of very fine sand to the size of marbles. They are generally rounded spheroids with a rough surface upon which small protuberances may occur. The proportion of such pellets is so large in many soils that agriculturists have applied the term "shot clays" to them. Bennett and Allison (1) called attention to the presence of iron pellets, locally called "perdigon," in many of the lateritic clays of Cuba. An investigation of the occurrence and of some of the properties of the shot soils of Washington has been undertaken because of the genetic as well as practical interest attached to the process of shot formation.

OCCURRENCE OF SHOT SOILS

Field observations have revealed the presence of shot in upland soils developed from both glacial and residual material. The pellets form under forests but are absent under prairie conditions. Shot are found in soils belonging to both the brown and gray forest soil groups but are absent in forested lowland soils where poor drainage occurs and are not generally found in soils that are excessively drained. The most abundant formation of shot occurs in soil with restricted internal drainage but where the movement of water in the soil is essentially downward. Where shot occur, the soils are invariably acid in reaction. Shot appear to be a natural development in the normal soil profile of the region.

CLIMATIC CONDITIONS OF WESTERN WASHINGTON

Records available in the region of shot formation indicate that the pellets form under an annual rainfall ranging from more than 120 inches to less than 20 inches. The exceptionally mild winter temperatures in the Puget Sound country allow an almost constant winter percolation to occur in upland soils. This contributes to the formation of well-leached, mature profiles. A dry period usually occurs near the middle of the summer season, which is signifi-

[1] Published as Scientific Paper No. 318, College of Agriculture and Experiment Station, State College of Washington.

cant because it brings about strong precipitation and dehydration processes within the soil and perhaps a reversal in the direction of water movements within the profiles.

The range in mean annual temperatures in localities below 1000 feet in elevation is small. While the mean for 48 stations averages 48.1°F., the variation from this mean is only about 3° either way. It seldom becomes extremely hot or extremely cold, the mean maximum temperature being about 58°F. and the mean minimum temperature about 38°F. The region is characterized by high relative humidities generally in the neighborhood of 80 per cent, although on summer afternoons it has been found to drop to 52 per cent. The average relative humidity of the air at all Puget Sound weather stations is 83 per cent.

FOREST COVER OF WESTERN WASHINGTON

The moist climate with relatively warm temperatures produces a heavy forest growth over practically all of western Washington. The most widely distributed tree is the Douglas fir (*Pseudotsuga taxifolia*), which makes up from 90 to 100 per cent of the forests up to an elevation of 1000 feet. In a narrow strip near the ocean, however, Sitka spruce (*Picea sitchensis*) is the dominant tree of the uplands. Associated with the Douglas fir, especially in local areas with slightly more than average ground moisture, are the true firs, lowland white fir (*Abies grandis*) and silver fir (*Abies amabilis*). Western hemlock (*Tsuga heterophylla*) occurs at higher elevations and in addition is often found occupying the more open areas where the Douglas fir has temporarily been eliminated because of natural causes. This replacement occurs because hemlock seedlings grow well in the rotten wood of fallen trees, the roots following the old tree trunk and completely permeating it. Seedlings of Douglas fir do not do this. In swampy places and on lower slopes where seepage occurs the Western red cedar (*Thuja plicata*) grows luxuriously. On many of the drier gravel plains lodgepole pine (*Pinus contorta*) establishes itself in nearly pure stands. On certain of the better soil types and especially where more than average amounts of organic matter are present in the soil, almost pure stands of red alder (*Alnus rubra*) occur. Cottonwood (*Populus trichocarpa*) may become thickly established in the river bottoms.

When the stand of Douglas fir is dense and well developed, scarcely any vegetative ground cover exists other than mosses and ferns, but when more light reaches the ground, a luxurious ground cover of shrubs and herbaceous plants is developed. Oregon grape (*Berberis aquifolium*), sallal (*Gaultheria shallon*), and huckleberry (*Vaccinium ovatum*) are the most common shrubs. The bracken fern (*Pteridium aquilinum pubescens*) is also widely distributed. Many species of mosses occur.

In spite of the luxurious forest growth there is a disappointingly small accumulation of forest mold. In certain old established Douglas fir forests known to be over 300 years old and presumably untouched by fires the mold

is only 1 or 2 inches thick. It is acid in reaction and relatively low in basic material.

PHYSICAL STUDIES OF THE SOILS

Quantity of shot in soils

Samples of the horizons of several soil profiles in western Washington were examined in the field during the dry summer season. The material was screened through a 2-mm. sieve with round holes. Gentle pressure with a rubber pestle was employed to break up the soil granules and to crush everything except the coarse gravel and the shot. After the coarse gravel was separated from the shot by visual selection, the three fractions were weighed. The results are presented in table 1.

The results show that there is no definite zone in all profiles where the greatest formation of shot takes place, although in three glacial soils the maximum development occurs in the region from 8 to 20 inches. One soil shows a maximum development in the 3-12 inch layer and one in the surface layer. In the latter case, however, conditions were not conducive to strong shot formation. In the residual soils the maximum shot development was found in the upper layers with decreasing numbers below a depth of 12 inches.

In these profiles, the greatest accumulation of shot occurs in the Kingston loam, which is underlaid by dense, impervious, brownish gray glacial drift. The weakest shot formation occurs in the Everett sandy loam soil, which is underlaid by open stratified gravel beds. These observations indicate that there is a stronger tendency for shot to form when the water movements within the profile are restricted.

Because of the marked similarity in forest and vegetative ground cover where these profiles were examined, no indications regarding the effect of these factors could be observed. The almost identical reaction, as indicated by similar pH values as determined in the field, implies that this factor is not a satisfactory explanation for differences in intensity of shot development.

The variation in size of the larger shot is indicated in figure 1 of plate 1, in which the largest individual measures about 19 mm. in diameter. The appearance of the larger shot, as they are embedded in the matrix of soil, is illustrated in figure 2 of plate 1, in which the three lumps from left to right represent the surface, subsoil, and clay substratum horizons in a profile. The granular character of the upper two horizons, due to the presence of these pellets, is clearly indicated. Figure 3 of plate 1 shows the effect of the rain in a road cut through a shot-bearing silt loam soil. The pellets protect the soil beneath them from washing and appear as caps on the soil columns left intact.

Mechanical composition

Representative samples of shot of all sizes larger than 2 mm. in diameter were selected from weathered horizons of several profiles and subjected to a long continued treatment with weak hydrochloric acid on a steam bath to break

TABLE 1

Percentage of shot and of coarse gravel larger than 2 mm. in diameter present in different horizons of several soil profiles in western Washington

The last horizon in each case is parent material

SOIL TYPE	HORIZON	DEPTH	SOIL	SHOT	COARSE GRAVEL
Glacial group					
		inches	*per cent*	*per cent*	*per cent*
Kitsap silt loam	1	0–8	84.4	15.6	0.0
	2	8–20	69.6	30.4	0.0
	3	20–	99.5	0.0	0.5
Alderwood loam	1	0–3	58.0	12.0	30.0
	2	3–10	49.0	26.0	25.0
	3	10–20	52.0	29.0	19.0
	4	20–28	56.0	25.0	19.0
	5	28–	58.0	0.0	42.0
Alderwood sandy loam	1	0–3	67.0	30.0	3.0
	2	3–12	60.0	33.0	7.0
	3	12–24	61.0	27.0	12.0
	4	24–	52.0	0.0	48.0
Kingston loam	1	0–2	65.0	27.0	8.0
	2	2–8	33.0	50.0	17.0
	3	8–20	32.0	65.0	3.0
	4	20–28	77.0	0.0	23.0
	5	28–	50.0	0.0	50.0
Everett sandy loam	1	0–4	59.0	2.0	39.0
	2	4–12	48.0	1.0	51.0
	3	12–24	40.0	0.0	60.0
	4	24–30	50.0	0.0	50.0
	5	30–	34.0	0.0	66.0
Residual group					
Olympic clay loam	1	0–8	53.0	47.0	0.0
	2	8–20	54.0	46.0	0.0
	3	20–30	65.0	31.0	4.0
	4	30–42	98.0	0.0	2.0
	5	42–	90.0	0.0	10.0
Wind River loam	1	0–4	60.0	40.0	0.0
	2	4–12	62.0	38.0	0.0
	3	12–20	65.0	35.0	0.0
	4	20–36	70.0	30.0	0.0
	5	36–	89.0	0.0	11.0
Underwood loam	1	0–4	51.0	49.0	0.0
	2	4–12	46.0	54.0	0.0
	3	12–24	71.0	29.0	0.0
	4	24–36	94.0	6.0	0.0
	5	36–	100.0	0.0	0.0

them down. A concentration of about 3 per cent of acid was required before disintegration occurred, and from 1 to 8 per cent of the original weight of the shot was lost through solution processes. After complete breakdown the acid was filtered off, the residue washed with water and then placed in a dispersion machine together with an excess of sodium hydrate solution. After dispersion the percentages of the various soil separates were determined by the hydrometer method of Bouyoucos (2) and by screens. Samples of the soils

TABLE 2

Mechanical composition of the disintegrated shot larger than 2.0 mm. in diameter and of the corresponding soil from which the shot were screened

SOIL	HORIZON AND SAMPLE	PERCENTAGE IN DIFFERENT SIZE GROUPS (DIAMETERS IN MM.)							
		>2.0	2.0–1.0	1.0–0.5	0.5–0.25	0.25–0.10	0.10–.005	0.5–0.05	0.005—
Kitsap silt loam	1 shot	1.35	2.01	3.55	5.65	13.77	17.57	25.30	31.05
	2 shot								
	1 soil	0.00	1.69	4.87	2.03	13.54	11.72	16.10	50.05
	2 soil	0.00	1.79	4.91	2.58	9.68	16.89	20.20	43.95
Kingston loam	1 shot	0.00	0.49	3.73	3.65	9.84	9.56	57.11	15.62
	1 soil	8.00	1.26	4.97	6.86	31.04	24.09	16.83	14.25
Clallam sandy loam	1 shot	38.40	3.15	3.78	4.10	10.84	4.70	50.11	23.32
	1 soil	20.00	9.28	16.32	8.50	14.23	7.57	28.02	16.08
	2 shot	26.80	7.80	9.04	7.21	9.79	8.80	36.54	20.82
	2 soil	18.00	8.02	16.18	10.10	16.05	8.75	24.02	16.88
Alderwood sandy loam	2 shot	23.00	1.76	4.83	4.70	14.23	36.10	16.56	19.85
	2 soil	7.00	9.14	11.36	5.52	19.75	20.88	17.64	15.70
	3 shot	20.0	3.06	4.50	3.97	13.45	26.65	31.47	16.90
	3 soil	12.0	11.22	12.72	7.29	16.26	15.68	22.14	14.81
Wind River loam	2 shot	3.20	0.40	4.22	6.94	24.74	31.88	19.14	12.68
	2 soil	0.00	2.82	8.17	6.64	26.49	10.51	22.96	22.40

which surrounded the shot in each horizon were similarly analyzed. The results of these studies are presented in table 2.

The analyses bring out an interesting characteristic of the shot material by showing that coarse gravel particles may act as nuclei for shot formation. In two samples where coarse gravel was naturally present in the soil, a larger amount occurs in the disintegrated shot; and in two cases where the soil contained no gravel the shot, when broken down, released such particles. One soil, of those analyzed, behaved in exactly the opposite manner. A large pro-

portion of the shot from the Alderwood sandy loam soil had gravel nuclei, whereas the shot from the Kingston loam soil were entirely free from them. These coarse particles apparently became cemented into the pellets and were again released during the acid digestion.

Microscopic observations during the screening of the sand fractions indicated that shot occur in the fine sand separates from all the weathered horizons but do not appear in the very fine sand fraction. This indicates that shot may also start as small aggregates and apparently grow as weathering proceeds.

In five of the eight horizons examined, the disintegrated shot contained more of the silt separate than the corresponding soil. In the other three horizons there was more clay in the disintegrated shot than in the soil. It is possible that the acid digestion used to break up the shot may have influenced this, but since the solution processes mainly attacked the cementing material of the shot aggregates, some indication is given of weathering trends since the time of cementation of the shot.

CHEMICAL ANALYSES

Samples of soil and shot from several horizons were ground to pass a 100-mesh screen, dried, and then fused with anhydrous sodium carbonate in the usual way. After solution of the cake with hydrochloric acid and the removal of silica, the determinations of total silica, sesquioxides, calcium, magnesium, and phosphorus were carried out according to official methods. The J. Lawrence Smith fusion of the same samples was employed to obtain data regarding total sodium and potassium. The results of these analyses are presented in table 3.

The data in table 3 indicate that the chemical composition of the shot is different from that of the soil in which they were formed. The silica content of the shot is always lower than that of the corresponding soil. At the same time, the sesquioxide content of the shot is proportionally greater than that of the soil. Associated with this increase in iron and aluminum is a strong enrichment of the shot in phosphorus. From two to five times more phosphorus is contained in the shot than is found in the soil. The enrichment of the shot in sesquioxides indicates also that this material is probably the cementing material holding together the finer components of the shot. The dark color exhibited by a freshly broken shot pellet suggests that iron compounds are chiefly responsible. It is likely that the sesquioxides and phosphates in solution as a result of the weathering of the primary minerals precipitate and then become dehydrated during the dry summer season and, being difficult to redissolve in this condition, they function as permanent cementing material in the shot. The original concentration of quantities of the soluble iron and aluminum compounds around the shot nuclei probably occurs during the early stages in the drying out of the soil. There is not much consistency about the comparative base content in the shot and soil samples, for sometimes the shot and sometimes the soil is richer in calcium, magnesium, sodium, or

potassium. The large variations in relative proportions of the silica and the sesquioxides probably influence the apparent percentage of basic material considerably.

In view of the fact that no definite clay concentration layer and no definite B horizon exists in any of the soil profiles in western Washington that have thus far been analyzed and because of the similarity in the analyses of shot and of B horizons reported for brown and gray forest soils elsewhere, it is reasonable

TABLE 3

Chemical composition of the shot larger than 2.0 mm. in diameter and of the soil from which the shot were screened

(Total solution analyses)

SOIL	HORIZON AND SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	Ca	Mg	Na	K	P
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Kitsap silt loam	1 shot	56.52	22.62	9.98	1.38	1.62	1.67	1.46	0.439
	1 soil	57.14	20.31	7.98	1.60	1.92	1.53	1.28	0.169
	2 shot	61.45	19.58	7.97	1.60	1.26	1.96	1.40	0.229
	2 soil	65.27	16.81	7.19	1.80	1.74	1.92	1.22	0.047
Kingston loam	1 shot	65.97	17.77	5.83	1.75	1.09	1.88	0.96	0.277
	1 soil	75.30	12.57	3.43	1.80	0.87	2.19	1.02	0.128
Clallam sandy loam	1 shot	61.75	18.97	7.98	2.05	1.36	1.96	1.01	0.945
	1 soil	69.86	15.16	4.79	2.27	1.14	2.15	1.04	0.250
	2 shot	64.20	17.62	7.58	2.02	1.29	2.01	0.98	0.628
	2 soil	71.15	13.92	5.43	2.32	1.19	2.32	1.04	0.270
Alderwood sandy loam	2 shot	58.52	18.52	10.38	2.35	1.69	1.97	1.01	0.479
	2 soil	77.50	9.51	4.79	1.85	0.86	2.09	0.99	0.129
	3 shot	62.65	13.08	9.82	2.45	1.47	2.19	1.03	0.263
	3 soil	73.75	12.87	5.03	1.90	1.00	2.02	0.99	0.128
Wind River loam	2 shot	52.35	25.12	8.78	2.40	1.11	1.83	1.24	0.270
	2 soil	58.46	21.03	7.97	2.20	1.09	2.35	1.38	0.118

to look upon the shot pellets in western Washington soils as portions of a diffused B horizon. In place of the usual development of a distinct layer with a reduced silica content and an enriched sesquioxide supply, the B horizon in western Washington soils forms as pellets around suitable nuclei throughout the entire profile. The conditions which cause this unusual development are no doubt the extreme drying out of the soil profile in summer, thus throwing out of solution and dehydrating the soluble iron and aluminum compounds and rendering them relatively insoluble and stable. These materials act as

the cementing agents for the shot aggregates. The more restricted the internal drainage and the less the removal of the soluble iron and aluminum compounds by leaching, the more intense is the shot formation. The shot differ, however, from ortstein because they do not contain so much organic material as is ordinarily associated with this development.

The presence of such a large percentage of phosphorus in the large shot raises an interesting question regarding analytical procedure for the chemical analyses of shot soils. In the case where 60 per cent of the total soil mass is screened out as shot larger than 2.0 mm. in diameter and these shot contain five times more phosphorus than the soil which is left for analysis, it becomes an important question to know whether the phosphorus of the shot is available to plants. If it is, then the arbitrary discarding of a large proportion of the soil, by screening, will result in obtaining entirely misleading data on the phosphorus situation in that soil. Extraction studies with the shot in their natural condition revealed that at pH 2.0 a large amount of phosphorus is readily brought into solution, and, although the surface area of the large shot in the samples was small, strong concentrations of soluble phosphorus were obtained from them in a short extraction period. This indicated that the available phosphorus contained in the shot could not be ignored.

A preliminary experiment with tomatoes growing in quartz sand cultures was then undertaken. A number of containers were filled with quartz sand alone, and duplicate sets were mixed with 10 per cent of the following phosphorus carriers—rock phosphate, ground shot (100 mesh), and whole shot (2.0 mm. and larger). A nutrient solution containing no phosphorus was furnished daily to the plants set in each container, having a phosphorus carrier; and for comparison two jars with quartz sand alone received a complete nutrient solution with phosphorus. The results after 8 weeks' growth are shown in figure 4 of plate 1.

The phosphorus of the shot is evidently available to tomato plants. This and the extraction experiments make it imperative to give consideration to the shot in western Washington soils when studies of available phosphorus are being made.

GENERAL DISCUSSION

Chemical analyses of the soils indicate that podzolic soil formation processes have been active in the development of the profiles. This is apparently the dominant process in the forested area on the west coast of Washington. Under the acid condition within the profiles, the iron and aluminum minerals are readily attacked and made soluble. The dry summers, however, inhibit a general downward movement, and no clean cut B horizons are produced. Perhaps because of the abundance of these compounds and their evident activity as cementing substances upon dehydration, their precipitation takes place in part at least around localized nuclei furnished by coarse particles in some cases or by other focal points. The surrounding soil material is fastened

together by this cementing action. Since small shot are encountered in all of the sand fractions down to fine sand, decreasing in proportional amount as the size diminishes, many shot must start other than around a gravel nucleus. In effect the soils of the region have their B horizon scattered throughout the entire profile rather than occurring as a definite horizon. Although individual shot pellets resemble rounded ortstein fragments to some extent, they are too low in organic matter to permit the ortstein designation. They are more similar to the semi-cemented materials of the B horizons of podzolic soils like the Fox series of the central states.

SUMMARY

An investigation of the occurrence and of certain physical and chemical characteristics of shot clay soils in western Washington has been made. The results may be briefly summarized as follows:

Shot clays are formed under forest vegetation only and are best developed where there is restricted internal drainage in the profile. They appear to be a natural development in the normal profile of the region.

The proportion of shot in the glacial soils increases with depth in most cases and then decreases again. In the residual soil group most of the shot are found in the upper layer and decrease in numbers with depth (table 1).

The size varies from 0.05 to 19 mm. in diameter in the soils examined. The shot are spheroidal in shape.

Coarse gravel is often found in the center of the larger shot, but the smaller pellets appear to be aggregates of finer soil particles.

The shot often contain more silt and less clay than the surrounding soil matrix, but no striking differences in the percentage of sand separates occur. This might indicate that at the time of cementation the soil was richer in the silt fraction, but, upon further weathering, much of the unconsolidated portion of the soil outside of the pellets has been broken down to the dimensions of clay.

The shot are richer in the sesquioxides and in phosphorus than is the soil surrounding them. On the other hand the soil is richer in silica than are the shot. Phosphorus in particular is concentrated in the shot.

A possible explanation for the formation of these pellets is suggested by the precipitation and dehydration of soluble iron and aluminum compounds around nuclei during the dry summer season. The low solubility of the sesquioxides and phosphates subsequent to dehydration produces a permanent cementing material.

Because of the similarity in composition of B horizons in normal podzolic soils and of shot in western Washington soils, it is reasonable to consider the shot as parts of a diffused B horizon scattered throughout the weathered portion of the soil profile.

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PLATE 1

FIG. 1. Soil shot from western Washington. The maximum diameter of the largest specimen is 19 mm.

FIG. 2. Typical lumps of shot clay soil, showing the larger shot embedded in the soil matrix. The lump at the left is from the surface soil, the middle one from the subsoil, and the lump at the right is from the clay substratum and contains no shot.

FIG. 3. The appearance of soil shot in a rain washed road cut, showing columns of soil each capped with a shot which protected the soil from being washed away beneath it.

FIG. 4. The appearance of tomato plants after 8 weeks' growth in sand culture, which received the following treatments: *OP*, nutrient solution without phosphorus; *CN*, complete nutrient solution with phosphorus; *RP*, nutrient solution without phosphorus—10 per cent rock phosphate in sand; *GS*, nutrient solution without phosphate—10 per cent ground shot; and *S*, same with 10 per cent whole shot.

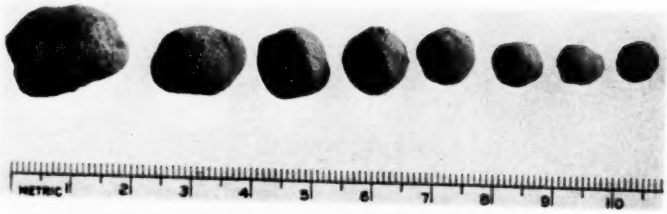

FIG. 1

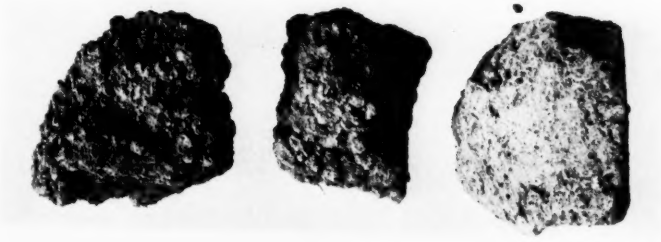

FIG. 2

FIG. 3

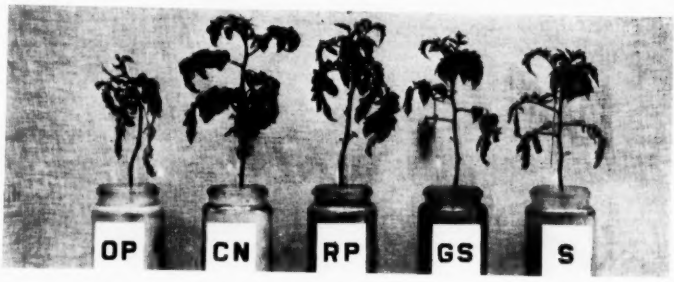

FIG. 4

UNIV. OF MICH.

A STUDY OF THE PRACTICABILITY OF THE WALKLEY AND BLACK METHOD FOR DETERMINING SOIL ORGANIC MATTER[1]

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Received for publication May 21, 1935

The need for a rapid approximate method for organic carbon determinations in soils which can be depended upon to give comparable results has long been recognized, and several investigators (3, 4, 5) have endeavored to fill this need. The recently published work of Walkley and Black (7) gives promise of more nearly meeting the requirements of such a method than any previous one. It was considered of interest, therefore, to investigate the practicability of the Walkley and Black method by comparing it with the wet combustion method in which are used various soil types to which known quantities of organic matter have been added in the form of straw.

The seven soil types used in this work were selected for their wide differences in origin, physical characteristics, organic matter content, and location. These are listed in table 1.

Gravel and foreign material were thrown out, and the soils were sieved through a 60-mesh screen and oven-dried at 105°C. for 12 hours. Each soil was divided into three portions, two portions being weighed and thoroughly mixed with 1 and 2 per cent, respectively, of finely ground straw which had also been sieved through a 60-mesh screen. The total carbon contents of these samples were run by the Walkley and Black method (7) and also by the A. O. A. C. wet combustion method (2). Since various investigators (1, 8) have found that the dry combustion and the wet combustion methods give similar results, the latter was selected because of its convenience.

The carbon content of the straw was 43.5 per cent as determined by the wet combustion method. No attempt was made to determine the carbon in the straw by the new method because the high carbon content of this material necessitates the use of such exceedingly small samples that accurate results are difficult to obtain.

The carbon contents of the seven soil types as obtained by the two methods are given in table 2.

The results obtained by the two methods agree very well for the Melbourne,

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Palouse, and Everett soils. The Chehalis, Puget, and Spanaway soils gave high results by the new method. The results for the Ephrata soil were satisfactory for the check soil but much too high when straw was added.

TABLE 1

Description of the soil types used

SOIL SERIES	CLASS	LOCATION IN WASHINGTON	PARENT MATERIAL	ORGANIC MATTER*
				per cent
Spanaway	Sandy loam	Central western	Glacial, outwash plain	4.08
Everett	Gravelly sandy loam	Northwest	Glacial till	4.49
Puget	Silt loam	Northwest	Alluvial, outwash of glacial	3.56
Melbourne	Silty clay loam	Southwestern	Residual	5.06
Chehalis	Silty clay loam	Southwestern	Alluvial, outwash of residual	4.62
Ephrata	Very fine sandy loam	Central	Alluvial, river terraces	0.49
Palouse	Silt loam	Southeastern	Loessial	2.50

* As determined by A. O. A. C. wet combustion method.

TABLE 2

Comparison of the organic carbon contents of seven soil types as determined by the wet combustion and the Walkley and Black methods

SOILS	CHECK				1 PER CENT STRAW ADDED				2 PER CENT STRAW ADDED			
	Wet combustion	Walkley and Black C × 1.32	Walkley and Black*	Recovery†	Wet combustion	Walkley and Black C × 1.32	Walkley and Black*	Recovery†	Wet combustion	Walkley and Black C × 1.32	Walkley and Black*	Recovery†
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Spanaway sandy loam	4.08	4.38	3.29	80.6	4.41	4.75	3.56	80.7	4.76	5.17	3.88	81.5
Everett gravelly sandy loam	4.49	4.56	3.42	76.2	4.87	4.99	3.74	76.8	5.22	5.44	4.08	78.2
Puget silt loam	3.56	3.97	2.98	83.7	3.98	4.52	3.39	85.2	4.34	4.85	3.64	83.9
Melbourne silty clay loam	5.06	5.08	3.81	75.3	5.50	5.55	4.16	75.6	5.86	5.93	4.45	75.9
Chehalis silty clay loam	4.62	4.85	3.64	78.8	5.03	5.35	4.01	79.7	5.44	5.68	4.26	78.3
Ephrata very fine sandy loam	0.49	0.49	0.37	75.5	0.93	1.02	0.77	82.8	1.27	1.53	1.15	90.6
Palouse silt loam	2.50	2.33	1.75	70.0	2.90	2.82	2.11	72.8	3.32	3.34	2.51	75.6

* Conversion factor, 1.32, omitted.

† By Walkley and Black method (conversion factor omitted) based on results of wet combustion method.

Because of the consistency of the approximate method in giving nearly parallel but slightly higher results than the wet combustion method it appears that the former method accounted for nearly all the straw added. This is

indicated also in table 2, which shows the percentage of carbon recovered by the new method, the wet combustion method being used as the standard and the correction factor proposed by the authors of the new method being omitted.

It is apparent that soil type influences the percentage recovery of the total carbon present, but for western Washington soils, for any one type with its varying organic matter additions, the percentage recovery is approximately the same. The central and eastern Washington soils, however, are not so consistent.

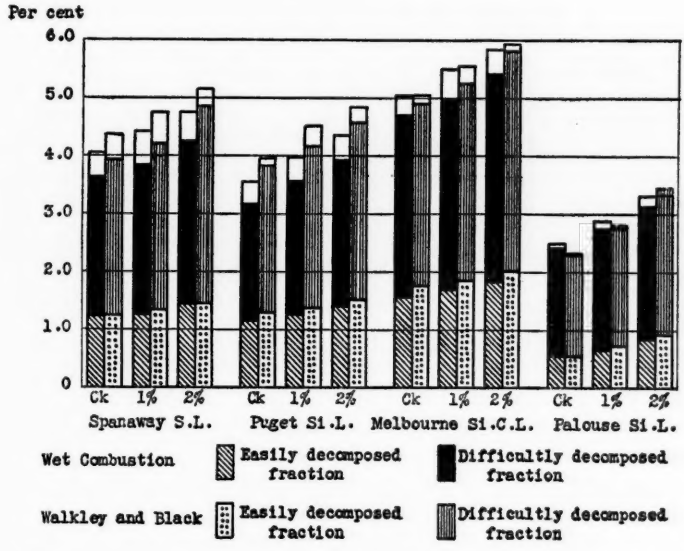

FIG. 1. THE EASILY AND DIFFICULTY DECOMPOSABLE FRACTIONS OF SOIL ORGANIC MATTER, IN PER CENT CARBON, AS DETERMINED BY THE WALKLEY AND BLACK AND THE WET COMBUSTION METHODS ON FOUR SOILS, EACH UNTREATED AND TREATED WITH 1 PER CENT AND 2 PER CENT STRAW AS INDICATED

Unshaded portions represent difference between the sum of the fractions and the total in original soil.

Since Walkley and Black (7) found an average of 76 per cent recovery of the total carbon in the soil by their method, they assumed that there is a definite fraction of organic matter common to many soils which is readily attacked by oxidizing agents. By removing the simpler organic fractions from the soil and separately determining the carbon in the soil residue and in the organic fraction removed, it might be possible to determine in which fraction the disagreement of the two methods lies. The soils were treated with 80 per cent sulfuric acid, as worked out by Waksman and Stevens (6). This treatment removed the starches, hemicelluloses, and celluloses by filtration and washing with hot water. Lignin and lignin-like materials were left in the soil. The

filtrate was reduced to a definite volume, and aliquots were used for determining the total carbon content. Total carbon was also determined on the treated soil residue. The results for four soils are graphically represented in figure 1.

Of the four soils studied, three—Spanaway, Puget, and Melbourne—were from western Washington; and the other, Palouse, was from southeastern Washington. The two methods agree fairly closely for the simpler organic fraction; i.e., starches, hemicellulose, and cellulose extracted by the use of 80 per cent sulfuric acid. Since the agreement is so close, it may be assumed that it is not these fractions which give the observed differences between the two methods for the original soils.

When the results of the two methods are compared for the more resistant fraction of the organic matter they are shown to be in about the same ratio as in the unfractionated soil. This would seem to indicate that the major differences in the results by the two methods originate in the more resistant fraction of the organic matter. It is also possible that some of the observed differences may be due to the presence of inorganic oxidizing or reducing substances as suggested by Walkley and Black (7).

TABLE 3

Effect of alkali carbonates on method

	OFFICIAL			WALKLEY AND BLACK
	Total C	CO_3 C	Organic carbon	
	per cent	*per cent*	*per cent*	*per cent*
Soil No. 1	1.728	0.534	1.194	1.32
Soil No. 1 + Na_2CO_3	2.470	1.282	1.188	1.31
Soil No. 2	0.444	0.099	0.344	0.40

EFFECT OF CARBONATES IN THE SOIL ON THE WALKLEY AND BLACK METHOD

Since this method is not dependent on CO_2 evolution no correction is necessary for inorganic carbonates in the soil, and, therefore, the method should be well adapted for determining the approximate organic matter content of soils containing carbonates. The data presented in table 3 are averages of closely agreeing duplicate determinations, and although they do not cover a wide range of soils the results bear out this assumption. The relationship of the results obtained by the two methods on these soils is very similar to that of the results of the other seven soils considered in this study. Thus this method may have particular merit for use with soils containing carbonates where time is a factor and absolute accuracy is not essential.

SUMMARY

A comparison was made of the Walkley and Black approximate method with the wet combustion method for the determination of organic carbon in seven widely different soils, portions of which received 1 and 2 per cent of straw

respectively. The organic matter in four of these soils was fractionated by extraction with 80 per cent sulfuric acid, and the organic carbon in the two fractions was determined separately by both methods. The effect of carbonates on the new method was also briefly considered.

The results obtained by the approximate method are slightly higher than those obtained by the wet combustion method but in general they are parallel. The approximate method accounts for practically all of the organic matter that was added in the form of straw.

When the organic matter was divided into the easily and difficultly decomposed fractions the results of both methods agreed very well for the former, but the same general differences observed for the results on the unfractionated soil were found in those for the difficultly decomposed portion of the organic matter. Probably the more resistant forms of organic matter and possibly certain oxidizing or reducing substances present in the soil are responsible for the higher results obtained by the approximate method.

The Walkley and Black method is adapted for determining the approximate amount of organic matter in soils containing inorganic carbonates without correcting for their presence.

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DIRECT MICROSCOPIC AND BACTERIOLOGICAL EXAMINATION OF THE SOIL

GIACOMO ROSSI

ASSISTED BY

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Received for publication May 29, 1935

The object of this paper is to summarize in English the methods previously published by the writer (3–12) in Italian and German and to explain the most important results obtained with these methods.

METHODS ADOPTED IN OBSERVATIONS

Preparation of the soil sample by impression

Although the impression method is now somewhat out of favor as compared with the preparation of the soil sample by crushing, to be described later, it seems advisable to refer to it, as it is still of certain value in many cases. In putting it into practice a kind of soil impression apparatus is employed. This is essentially a device to hold a microscope slide in such a manner that it can be pressed against the surface of soil. At first the writer smeared this slide with a solution of agar or gelatin, but the present technic uses a clean slide thoroughly sterilized by being passed 50 times over a flame or, when considered necessary, also treated with distilled water.

The material remaining attached to the slide is then fixed by heat in the usual way, stained by the Conn method with carbol erythrosin (1 per cent erythrosin solution with 5 per cent phenol) employing heat, and thoroughly washed and dried.

In the case of a heavy soil, this slide is pressed against a fresh cut made with some sharp instrument. With a sandy or crumbly soil it is necessary, however, to prevent any lateral slipping. To this end metal sheets may be used with a sharp cutting edge and forcibly driven into the soil with a mallet, in this way marking out on three sides a parallelepiped of ground. Next, with another squared sheet corresponding in width to the median of the three sheets previously driven into the ground, the soil immediately above the layer which is to be sampled is lifted off, naturally after removal of the soil in front so as to ensure free space for the operation.

The soil impression may be taken parallel to the surface or obliquely or against a perpendicular face; the results do not vary greatly especially if the impression is taken at a certain depth. Impressions made at the surface are not satisfactory.

Preparation by crushing

For the crushing method a small lump of soil is crushed on the surface of a microscope slide. The crushing takes place without artificial means when the soil is sufficiently soft; otherwise, the selected fragment is placed on a glass or a porcelain slab and then sprinkled with as much distilled water as it is considered capable of absorbing; for this a few minutes will suffice. It will then be easy to obtain preparations by impression (Klatsch Preparat).

In many cases the crushing can be done between a pair of slides without using the apparatus. The drying process can be carried out before separating the two slides, and thus two prepared slides can be obtained simultaneously.

The microscopic examination in all cases is made with the objective in immersion, the preparation being covered with a slip or the oil being run directly on the preparation.

Observation of the lower face of the preparation

It is often desirable to study the lower side of a preparation as well as the upper side. In doing this a cover slip is prepared and stained by the method described hereinafter for counting cluster forms (golumerles). After the cover slip has been fixed with cedar oil on a slide with the oil between the upper face of the slide and the lower soil-free face of the cover slip, it is then examined with an objective immersed in another drop of cedar oil on the soil side of the cover slip. An easily recognizable field is then found and carefully studied, after which the cover slip is detached from the slide and replaced with the other side up, *rotating about one of its sides which is parallel with the longitudinal side of the slide.* One then has to locate the same field examined with the other side up. This is sometimes difficult but can usually be done with the assistance of marks made on the stained cover slip with a needle dipped in a violet dye. Especially valuable in relocating the field is a rough sketch of the field in question drawn on transparent paper which can be turned upside down to show the appearance of the desired field when it is to be studied in its second position.

Method of counting the cluster forms

The count of the groupings or accumulations reveals cluster forms far more frequently, as we shall see. To this end, from a very summary method based on the number of clusters present in 16 fields of the prepared slide, we have, with the aid of an expert mathematician,[1] developed one far more accurate which is carried out in the following way:

A number of ordinary glass cover slips are weighed and, to keep them distinct from one another, are placed on numbered squares on a sheet of paper. Each slip is then covered with small lumps or fragments of soil which are moistened to their full absorption capacity. Crushing is then accomplished

[1] Giovanni Candura.

with a slide or by means of the soil impression apparatus. After drying, the cover slips are stained in 1 per cent erythrosin dissolved in 5 per cent phenol, heated to steaming over a flame, washed in cold water, and dried over the flame. Each cover slip is then weighed again, the difference between this weight and the previous one giving the weight of the attached soil. The cover glass is then attached to a slide and examined under oil immersion. The clusters present in 20 fields are counted.

The Candura formula (5) is then applied, that is: taking P as the weight of the soil in grams, S as the area of the soil sample in square centimeters (*i.e.*, the area of the whole coverslip holding the soil sample), s as the ratio $\frac{S}{P}$ (specific area of the soil), a as the number (*viz.*, 20, as already stated) of the fields observed, N as the sum[2] comprehensive of the clusters seen in a fields, n the ratio $\frac{N}{a\ \pi r^2}$, that is the number of clusters per centimeter, we shall obtain:

$$n\ s = A$$

that is to say, A will be the number of the cluster forms per gram of soil.

In employing this method it is convenient to use two, four, or eight (usually four) series of 15 cover slips each and to apply the Candura formula to each slide. The fewer the cluster forms in the preparation, the larger the number of series will be needed. The object is to make a sufficient number of determinations so that the figure obtained upon averaging the results from half the cover slips will be approximately equal to that of the other half. Further details and notes of difficulties surmounted may be found elsewhere (12).

METHOD ADOPTED FOR OBTAINING MATERIAL

At present one method only is in use, *viz.*, *burial of the slides*, which has been employed by the writer (1, 4, 5, 7, 13) since about 1927.

Pairs of slides may be buried at a greater or less depth and extracted after a given time; they are then stained in the same way as soil samples prepared by crushing. Experiments have shown that the soil bacteria pass over the slide both on the upper and on the lower face, and not only the schizomycetes but also the hyphomycetes, streptothrices, and protozoa.

It is necessary to use pairs of slides because one of the two faces—the lower face in the case of the upper slide and the upper face of the lower slide—must be put out of action by the necessity for staining and observation. In other words, the lower face of the lower slide acts as the lower face of the upper slide.

[2] The authors take this opportunity of pointing out that on p. 238 of our article (12) the value of N is erroneously given as that of the *area occupied by 1 gram of soil* instead of, as on p. 15 of the article (5) which, however, must be corrected definitively: *the sum comprehensive of the clusters seen in a fields.*

At the moment of burial the slides are passed through the flame 50 times in order to purify them of any substance which might have chemotactic action on the soil bacteria, *unless it is preferred to smear them with substances of which it is desired to study the possible chemotactic capacity.*

In dealing with natural soil *in situ*, and if the earth is compact and can be sliced, the apparatus we have described for taking soil impressions at a depth will serve very well. Having made the cut at the required depth, the pairs of slides are placed in position and covered as far as possible with the slices of soil taken from the cut, which are pressed gently into place. The opening made in front of the cut is also filled in, if possible replacing the earth in the same order in which it was removed. Particularly in dealing with grassy turf it is advisable to keep the surface sods intact, putting them back into position over all the disturbed area. It is not advisable to water in this case.

METHODS OF REPRESENTATION AND DESCRIPTION

One of the greatest difficulties in these studies is to convey what we have seen to other students who do not wish to verify our observations by repeating them. Illustrations have been given in color in previous articles, but are not reproduced here because of the expense. For the benefit of those who are interested in studying them and who have, or can obtain, the preceding articles, the eight plates previously published are referred to here (in Roman numerals) according to the following scheme:

Plate I (9, plate I); Plate II (9, plate II); Plate III (10, plate VI, and 5, plate I); Plate IV (10, plate VII); Plate V (3); Plate VI (11); Plate VII (8); Plate VIII (13).[3]

As to the method of reproduction, we naturally had not much liberty of choice between a drawing from the microscope and microphotography. Plates I to IV are examples of the drawings; and Plate V, fig. 10, 11, 12, and Plate VII, fig. 49 *a*, *b*, *c*, 50, and 51 are examples of the microphotography. The latter have been rendered more explanatory by coloring. These drawings are not claimed to be absolutely accurate reproductions because of three sources of error: first, the fact that the draftsman is not always scientifically trained; second, that the reproduction of color with artists' paints is not always exact; and third, that their reproduction in printing by the ordinary three-color plate method is still more difficult.

In the preparation of these drawings we have preferred a magnification of 750 diameters rather than one of 2,000 diameters as employed by Winogradsky.

Morphological observations made over a period of approximately 8 years on the groupings of schizomycetes and other microorganisms visible in the soil can be summed up in the following way, and the groupings themselves may be classified morphologically as will be shown later. It must, however, be premised that by the term *colonies* we mean something which has practically nothing in common with those which we are accustomed to find in agar gelatine

[3] *Sup. Proc. Internatl. Soc. Soil Sci.*

cultures, particularly because they are very much smaller and barely reach the size limits of the deep-seated colonies therein immediately after development.

Filmy colonies. These mainly consist of elongated schizomycetes (bacteria or bacilli), varying in length between 1.5 and 4.2μ and in breadth between 0.4 and 1.00μ (Plates: I, fig. 6; II, fig. 1; III, fig. 1 and 4; V, fig. 6; VII, fig. 45, 46, 47, 48_1, 48_2, 48_3). Although for the most part microscopic, colonies are often found as large as the field of the microscope itself (eg., diameter 220μ); hence, when complete and intact, they correspond to, or approximate, the size limits of the colonies deep-seated in agar cultures.

They all resemble the bacterial *films* of varying consistency, sometimes cartilaginous, which are formed on the surface of nutritive liquids. They too can be folded back—possibly by the action of the apparatus or generally of the manipulations—and the edges may be superimposed.

If an intercellular substance exists, it does not take the *erythrosin staining*. These colonies are sometimes visible to the naked eye, as may be seen in figure 10 of Plate II, on which is clearly shown the folding back, at times more than one fold apparently being present There exist forms which may be called "filmy colonies," which are not clearly disclosed by the microscope (ultra-microscopic colonies?) (Plate I, fig. 3). And still other forms exist resembling folded scraps, as though developed within the irregular openings between the mineral particles into which they fit.

Schizomycetic masses in cluster form. This is by far the most frequent form and the one we regard as characteristic of the soil in which it is found. These are the most frequent apparent types of the schizomycetes in the soil, and we have here an instance of groupings, which by their nature can never be of a large number of individuals (essentially of coccic or coccobacteric forms), because, in spite of many thousand observations, these groupings have *never* been found to assume any considerable proportions, except in the case of the *giant clusters* of which mention is made in another report (13) (Plate VIII, fig. 2 and 3). The number of constituent forms, so far as it is possible to count them, hardly exceeds 30; only when they assume the appearance resembling the embryological *morula*, forming compact masses, the number of individuals must be some hundreds. One of the largest areas is also reproduced in Plate V, fig. 3. It is not difficult to observe aspects which may very well be interpreted as points of transition from forms with a small number of individuals, and even of isolated individuals, to the *morula* form.

Now if 30 may be considered as the number representing the average maximum of microorganisms composing these groups, which from now on we will call *clusters*, or *glomerules*, the minimum number varies greatly and may even be supposed to be two only. There are fields in which the groupings are numerous with a varying number of components, but where there are also present isolated individuals (*e.g.*, Plate III, fig. 11). In this case one hesitates to assume that it is either a question of new clusters being formed, as it were, from parent clusters, or one merely of remains of larger clusters broken by the soil impression apparatus or by heat or by washing. It is difficult to admit that we have here merely remains of larger colonies, since as already stated *no colonies so large have ever been found.*

But in support of the view that the clusters have a morphological individuality formed only of few individuals as mentioned, there is the fact that in the large majority of cases, the *cluster* is not independent, as if it were superficially attached to a mineral fragment, but it is at the center of something which encloses it, as shown also in the figures of Winogradsky (14). The cluster, in fact, seems as though enmeshed in a membrane of plastic material which has been crushed under the action of the apparatus, opening the "envelope" and revealing the schizomycetic grouping, as shown in figures 6, 7, 8, 9, 10 of Plate III, less well marked on figures 1 and 2 of Plate V, and very well marked on figures 30 to 37 of Plate VII. In these last the appearance is exactly that of the schizomycetic cluster escaped from an envelope broken under the pressure of the apparatus. But even where there is no gap between schiz-

omycetes and the enclosing substance (and it is impossible to tell whether this space which appears to us to be void is really filled with material, which in contradistinction to the casing is *not stained*), it is clearly seen in figures 1 to 42 of Plate VII that all the clusters are immersed in a soft, and one may say, plastic substance. This substance appears to be differently stained from the schizomycetes, with that intensity of contrast which we are accustomed to note, *e.g.*, in the twofold staining of the acidophils or in histo-cytological stainings, and according to a chromatic scale which excludes only the colors of the most highly refracting part of the spectrum.

In counting the clusters of a field under examination, we have always conformed to the rule of neglecting the isolated forms, or those linked in twos or threes only, or even more, when in the same field there were also present more numerous groupings, or when the groupings reduced to a scanty number of individuals were assembled in "nests" not differing from those composed of numerous individuals.

As regards the form, there can be no doubt that the "coccic" is the prevalent form, but the *possibility must always be kept in view* that we may have, instead, cocco-bacteria, which are frequently found in conjunction with pseudo-cocci. A very variable characteristic, however, is the size even in the same preparation, as typically seen in Plate V, fig. 2.

There may rarely be found together (Plate III, fig. 7) cocci "nested" together, bacteria and bacilli with non-typical forms, and still more rarely (Plate III, fig. 6) a few individuals clearly of bacillar type "nested" like the cocci.

All these aspects occur if a thorough examination is made of the colored figures of Winogradsky.

Streptothrices. In contradistinction to Winogradsky, we have been able to discover these in the typical hyphic and stromatic forms (Plate II, fig. 3, Plate IV, fig. 6, and Plate V, fig. 12) and also to prove their presence by the use of the buried slides method.

Hyphomycetes. These we have found very frequently. An example is given on Plate II, fig. 3, and Plate VI, fig. 8. It frequently seemed quite easy to distinguish whether the forms under observation were dead or still living forms.

Other forms of schizomycetic colonies. These are quite rare, and we think (especially when dealing with soils that are rich in decomposing vegetable matter) that such of them as might be interpreted as special forms (*e.g.*, Plate II, fig. 2, and Plate V, fig. 9) are only filmy forms developed in special conditions, whether bacteric or bacillic, according to the distinction already made.

A particular form (which there is reason to believe is due to the same type of colonies and their components) is that made up of individuals with every probability and appearance of being spore-forming (Plate II, fig. 11, Plate III, fig. 1*b* and fig. 3, and Plate VI, fig. 2).

Very occasionally, groups have been found which appear to derive from the *remains of colonies* broken up by the soil impression apparatus, and made up of individuals suggesting the Amylobacters (Plate V, fig. 8) as not showing stain at the two extremities.

Protozoa. Protozoa in the form of cysts are found isolated, but, on the other hand, free protozoa (flagellate but also other forms) are found comparatively frequently grouped in masses which only the lack of accurate knowledge makes us hesitate to call "colonies" (Plate I, fig. 2; Plate II, fig. 5 and 12; Plate III, fig. 2; Plate V, fig. 11; Plate VI, fig. 1).

We have also, in all probability, observed casings of radiolar and foraminiferous forms in soils of undoubted marine origin.

Isolated forms. To what we have already said elsewhere on the subject, we can only add that, in soil strata other than the superficial layers, compact little "crowns" of *streptococci*, or possibly streptothrices, are often observed. Chains of *streptobacteria* are more rarely discernible.

We do not deny, however, that many other almost or entirely isolated forms may be found in the soil—in fact, they are frequent; but such observations as we feel justified in recording are the following:

1. The only formations which are numerous and are constantly present under the condi-

tions already specified and under those to which we shall later refer, are the filmy colonies and the clusters.

2. *All the others*, including the streptothrices, hyphomycetes, diatoms and protozoa, may be found sporadically and in some preparations in considerable numbers. These do not, however, form in the corresponding soil anything that can justify the view that they are an important or constant factor in determining its structure.

3. None of the isolated forms in small groups (such as the "crowns" of streptococci and thus coccic, bacteric, and bacillic forms) apart from the already described filmy and clustered colonies, take the form of *colonies* even as small as the filmy and clustered kinds.

Algae. Although we cannot deny the possibility that various unicellular algae may be found in the soil, we have identified numerous species, both on the surface and at comparatively deep levels, which undoubtedly suggest only the diatoms.

SIGNIFICANCE AND IMPORTANCE OF THE FILMY COLONIES

The observations made can be classified as follows:

1. Impressions of topsoils or of soils immediately below the layer of dead leaves, where this existed.

2. Impression made by raising the layers of moss or of lichens found either on the ground or on walls or trees, thus laying bare the layer immediately beneath.

3. Removal of plants from loose or soft soil, keeping the roots intact so that a small amount of soil is brought away with them, and an impression then taken of the larger among the small soil lumps thus obtained.

4. Excavation of the soil *in situ* and impression (or removal of small lumps) at depths of 5 cm., 10 cm., 15 cm., etc.

5. Making up of pots of soil mixtures, Vesuvian sand, and leaf mould, whether sieved or otherwise, in varying proportions. Examination after varying periods and in various conditions of preservation, particularly with regard to the water content.

By direct observation we have discovered the following facts:

1. By *impressing* superficial soil when the ground is damp and the plants fresh, we may note many bacilli all similar in type to those of the filmy colonies, and sometimes even filmy colonies themselves.

2. A similar result is given by lifting the layers of moss, hepaticas, and lichens in damp, shaded places and impressing the underlying mould.

3. The filmy colonies are in direct proportion to the quantity of organic matter in a state of decomposition in the soil under examination, to the weather, and to the temperature at which the soil mixture was prepared.

Giant filmy colonies found in pots holding a large proportion of leaf mould are reproduced in Plate VII, fig. 45, 46, 47, 48_1, 48_2, 48_3.

SIGNIFICANCE AND IMPORTANCE OF THE CLUSTERED COLONIES

Observational research

With the methods described and with all proper safe-guards, we have carried out two series of tests, one by observation and the other by experiment. The principal results obtained by simple microscopic observation and by counting the clusters are as follows:

Number and distribution of clusters in Italy. The smallest number of clus-

ters observed per gram of soil was 22,032 at Parco Gussone (Portici); the greatest, 13,416,699 at Benevente and 13,548,000 at Maccarese.

In both cultivated and natural soils the number of clusters tends to diminish with depth.

In ordinary arable strata (from 0 to 30 cm.) the numerical variations found in depth are of the same order as the numerical variations in extension.

Similarly in depth a given average of clusters generally holds good for strata of approximately 30 cm. thick.

In our experiments we have found the quantity of clusters to diminish from 10 to 20 million to a few thousand in descending from the surface to a depth of 1 meter.

Geographical distribution of the clusters. Winogradsky has already demonstrated, as the result of his research work from 1926 onward, that the microflora of the regions of the globe situated in the five continents does not vary greatly qualitatively, at least under direct microscopic examination. He did not, however, consider the matter of numbers, nor did Conn or Cholodny. It is our opinion that all previous research workers concerned themselves only with looking for *given forms* (the typical zoogloea) and must have tested soils from analogous strata, as the forms we have found and described prove that those of Winogradsky, Conn, Cholodny, et al. are not the only forms which are found and which may develop in the soil.

It may be added that in soil from the neighborhood of Hong-Kong we have found the same forms as in soils from other parts of the world and also in similar numerical series.

The soil clusters in relation to soil cultivation and the duration of cultivation. There is a remarkably clear relation between the *agricultural age of the soil* (by which is meant the number of years from which its human exploitation probably dates) and *the number of clusters.* The older the soil, the greater is the number of clusters; thus very few are found in soils the cultivable strata of which are only 28 years old, as at Parco Gussone (at Portici). For example, we find that soil (from Maccarese) which has a history of cultivation dating back some 3,000 years, gives 13,548,000 clusters per gram, whereas virgin soil (from Rive Pelate di S.Polo d'Enza) gives 412,119, and soil erupted from Vesuvius in 1906 has, to date, accumulated 40,392 clusters only.

The soil of a vegetable garden—one of those Neapolitan gardens which, with the aid of water, manuring, cleaning, and sun, gives five and six crops of superb products a year—was covered by Vesuvian ash in 1906 to a depth of about 25 cm. This ash was turned in, and as a result there was an increase in the number of clusters but so small as to be almost negligible when the numbers which are known to occur in rich soils are considered. This may indicate that the formation of clusters is a very slow process and *has no relation to the immediate productive capacity of the soil.*

Experimental research

Effects of physical agents on the cluster forms. The earlier research work consisted simply in placing the soils in which the clusters had been under examination, in a bacteriological thermostat for a longer or shorter period for the purpose of re-examination. It is then seen that a rise in temperature has an influence on the turgidity of the clusters and renders their staining brighter even in the space of only 40 hours.

Subsequently we had occasion to test two soil samples which had been left undisturbed in saucers containing a little water, renewed when evaporation seemed iminent. The saucers were covered with glass slips, but the closing was by no means hermetical; consequently, conditions remained undoubtedly aerobic all the time.

Examination of these soils after 7 years showed that under these conditions of humidity the clusters still remained, and one was observed (Plate VIII, figs. 2 and 3) which could only be defined as a giant type, so large that to sketch it two representations were necessary showing different focal levels.

This, together with apparent fragments of broken-up clusters observed suggested that the humidity had, so to speak, set up germination of at least part of the clusters, that is to say, a multiplication of individuals. Some of these individuals had subsequently been unable to carry out their normal chemical processes and had degenerated and disappeared. To investigate this point, direct experiments were carried on to note the action of water on the cluster forms under four distinct conditions of humidity as follows:

1. *Humidity at air saturation point* for which the soil samples were kept in closed containers with water on the floor of the container.
2. *Humidity at saturation point of the soil.* This result is obtained in practice by immersing the soil fragment in water, subsequently removing it, allowing it to drain, and then keeping it in a container such as the one previously described.
3. *Continuous immersion of the soil sample in water,* under the same conditions as the foregoing ones, with special precautions to prevent evaporation of the water.
4. *Natural humidity,* used as a control.

The results, which agreed fairly well in the majority of instances, showed that *humidity* in three cases gave a larger number of clusters (or a greater visibility due to the greater turgidity, according to our first observations?), but imbibition in three cases quickly reduced their number and with some delay in the fourth case, whereas the immersion process concluded by reducing very considerably the number in all cases.

Longevity and the preservation of the cluster forms in agricultural soil. It had already been known[4] for some time that the bacteria, including the non-

[4] See, *inter alia*, the enquiry of GILTNER, WARD, and LANGWORTHY, H. VIRGINIA 1916 Some factors influencing the longevity of soil micro-organisms subjected to desiccation, with special reference to the soil solution. *Jour. Agr. Res.* 5: 927–942, Abs. in *Centbl. Bakt.* (II) 49: 469 (1920). These writers attribute this phenomenon to the capacity of the soil for retaining moisture in hygroscopic form in as much as there seems to be no proportionate relation between the two phenomena. The prevailing clayey nature of the soil, on the other hand, would have an effect on the phenomenon.

sporing types, preserved their vitality for a long time in soil samples kept in the air.

For our own part, from 1930 onward, we ascertained that cluster forms readily taking erythrosin stain can be observed in soil samples of different degrees of age and preservation left on the shelves of the laboratory without any special attention.

In the tables given in the various reports, serial numbers are used to indicate the different samples which we have so far been able to observe. These have been proved to retain cluster forms even after 38 years of preservation in simple glass jars and even in open cardboard containers.

The number of the cluster forms for 50 microscopic fields varied from a minimum of 2 at 20 years of age to a maximum of 149 at 19 years of age, naturally in soils markedly different.

Action of agricultural operations on a small scale. An investigation was made of the effect of different methods of cultivation. The plots in this experiment were:

1. A plot lying fallow, which naturally acted as control;
2. A plot worked with a plough;
3. A plot worked by drilling implements (Marienburg drill);
4. A plot worked with various implements.

In other respects the plots remained alike for nearly 8 years.

The results of this experiment were all negative, none of the plots showing variations great enough to be regarded as of any significance.

Experiments with buried slides. In various contributions (3, 4, 10, 13) we have given accounts of a number of experiments carried out by the method described elsewhere in this report.

The results may be summarized as follows:

On the buried slides, in soils of all kinds, both bacterial clusters and filmy colonies may be found, especially on the lower face. Much more frequently are found the schizomycetes, both in isolation and grouped in ill-defined masses, hyphomycetes, streptothrices, and perhaps also desmobacteria and protozoa. There are also microorganisms that are difficult to classify, possibly including the mycobacteria of Krassilnikow (2a).

On smearing the slides with various solutions corresponding to fertilizing substances (such as sulfate of ammonia, asparagin, peptone, mannite, rice starch) in concentrations corresponding to such as would occur if used on the soil, no chemotactic effects were to be noted, apart from the influence of the starch, which brought about an abundant increase in the streptothrices and hyphomycetes of various forms, such as have been described in full detail in the articles already mentioned.

Certain groupings of hypho- and schizomycetes are clearly characteristic; the former seem to be lifeless and in process of destruction by the schizomycetes (Plate VIII, fig. 5).

There often appear on the slides what may be called "drop-forms" (sgocciolature). They are apparently produced by drops of moisture charged with bacteria coming in contact with either the upper or the lower surface of the slide and subsequently drying and leaving the bacteria attached to the glass.

The characteristic of these drop-forms is that they have not the least appearance of "*colonies.*" In a few very rare instances and only to a very small

extent, they suggest the filmy colonies described elsewhere, but in most cases they consist of schizomycetes of various kinds irregularly distributed, the prevalent forms being bacteria and bacilli, but also including *cocci*, which in the majority of cases are characteristically *very small indeed*. Sometimes (Plate VIII, fig. 8) a considerable doubt remains as to the category of organisms to which they should be properly assigned.

The so-called colloids and their behavior in regard to anilin staining. Winogradsky has called attention to the masses, probably of colloidal nature, which also stain with erythrosin in the slides stained to show bacteria and other microörganisms. We found such material to stain much less uniformly than the microörganisms, and in Plates II, V, and VII, we have shown it as staining red, red-yellow, yellowish, or yellow-gray. We have concluded that the shades of color seen in such material were not caused by the erythrosin but were either natural or the result of heating in the course of preparation. In support of this view we have described a certain number of slides contrasted with other unstained slides of the same soil and also of similar preparations treated under heat with a 5 per cent solution of phenol (as in the case of the Conn staining formula) but without any dye.

The colors are fairly uniform with each soil, fertilizers having no modifying effect.

Relations between the clusters and the absorbing root hairs. By various methods it was found possible to obtain fragments of roots and root hairs in the same preparation with the soil and the microörganisms therein. Such experiments showed no static or numerical relations between the clusters and the absorption apparatus of the plants, but the clusters were concentrated about the roots. The preparations made under natural or artificial conditions did not differ greatly from normal preparations in which roots, root hairs, and rhizoids had been intentionally or unintentionally introduced; they might or might not contain cluster forms like any other preparation; and, like any other preparation, they contained or did not contain filmy colonies, scattered bacteria, etc.

This was the first fact that led us to conclude that the cluster forms indicate a state of repose and not a trophic state on the part of the soil schizomycetes.

Specific identification of the flora observed under the microscope. An experiment has been carried out on the basis of which, after repetition and confirmation by other experiments, we should at least be in a position to deny to the cluster forms the character of Azotobacters.

From a seedbed containing sandy soil in which wheat grains have been placed to germinate, a seedling is uprooted, one of the branches of the radicle is deprived of the apical part, and the portion with abundant absorbent root hairs is divided into two parts.

One part is placed on an object glass, and water is added without crushing the plant material; it is left for a few minutes and then dried by means of a fan.

There is a considerable deposit of material which, observed under the microscope, contains:

Scattered *cluster forms*, some reduced and others typical and very pronounced.
Groups of *cocci* in chain form.
Small groupings or accumulations of delicate bacilli.
A very large number of tiny delicate bacilli, irregularly arranged, but observed only in a few fields. In all probability they develop from pre-existing colonies as a result of the water used in making the preparation.

The second portion is placed with all the soil attached in a test tube containing 10 cc. of distilled water, and well shaken. With the Hiltner and Störmer method (2b) and the processes described elsewhere (2), it is possible to determine the quantity of Amylo- and Azotobacters, and of ammonifying and denitrifying organisms, contained in the liquid derived from the suspension obtained.

The following results were noted:

Amylobacters.....none
Azotobacters.....none
Ammonifying organisms, not less than 1,000,000 and not more than 10,000,000
Denitrifying organisms, not less than 100,000 and not more than 1,000,000

Since the soil utilized was a good deal less than a gram (it was not praticable to weigh it because of the presence of the root and the impossibility of estimating the humidity), the positive numbers observed cannot be less than those actually existing.

This means that, after all, the flora seen under the microscope have, in all probability, no connection with living and trophic Azotobacters and Amylobacters. Since the other half of this sample had revealed under the microscope the presence of typical cluster forms, the connection of these with the Azotobacters is at least a matter of some doubt.

From such observations we have drawn the conclusion that the soil bacterial clusters may probably be considered as "cysts" functionally, analogous to those of protozoa.

This last conclusion is perhaps the most important. In so far as in a future more or less remote we might find ourselves obliged to assert that the bacteria observed by us in the soil are the only types or apparent types therein really discoverable, we now think it not illogical to suppose that in the stages of repose, a large number of the schizomycetes might tend to assume cluster-like forms, which for them would be stages of encysting, analogous to those of protozoa.

From these stages they would emerge when the soil-climate brought about modifications in the environment whereby (the cyst being, so to speak, opened) the bacteria would multiply with their characteristic rapidity, and would set up in turn that specific biochemical activity which distinguishes the species to which they belong. Although we do not claim that this is a strictly ac-

curate account, it is in any case certain that this principle of interpretation of the life history of the bacteria in the soil is borne out by the following observations:

The frequency and perhaps the universality of the cluster forms in agricultural soils;

The nearly constant form of the glomerular content, without excluding a diverse form of origin;

The relatively rare occurrence of the free bacteria in the soil;

The formation of filmy colonies wherever there is vegetable matter on the point of decomposing;

The demonstrated preservability of the soil cluster forms;

The analogy shown by the soil inhabiting cluster colonies with the colonies deep-seated in agar and gelatine cultures, an analogy which does not, however, go beyond the fact that both categories may take an almost similar form while belonging to widely differing species.

A similar interpretation leads besides to the better understanding of what is meant by a stage of equilibrium of the schizomycetic soil life, which we cannot conceive as one daily and ruthless struggle; and would tend to assimilate this life to the behavior of the protozoa, thereby unifying our concept of soil life.

Thus an explanation better than any at present available, could be given of the action, on the microbial flora, of irrigation, chemical manuring, green or stable manure, and, finally, ploughing; and a better explanation of the action of heat, cold, rain, and snow. The cluster schizomycetes would be like seeds which cultivation will cause to burst open at the proper moment.

CONCLUSIONS

The main conclusions that may be regarded as the result of all the work carried out so far by the authors in connecton with the direct examination of agricultural soils, may be summed up as follows:

The method of staining of the microorganisms in the soil with acid aniline stains (erythrosin, eosin), first discovered by Conn and employed by Winogradsky, may be used for obtaining direct images of the whole of the microflora (and also of a part of the microfauna) found in the soil.

By the use of special methods known as *soil impression and soil crushing methods* with variants, it becomes possible to identify in the soil the existence of special forms of *bacterial colonies*, nearly always microscopic in character, which we have described as *filmy and cluster-like.* The former predominate where organic matter on the point of decomposing is present; the second are present in greater abundance in proportion as the soil is "aged" from the agricultural point of view.

The method of *burial of slides* in the soil for periods of varying length has proved valuable for the study of the soil microflora.

The number of *cluster forms* is determinable by the special method of counting.

The isolated bacteria and the bacterial clusters in the ground can be stained even 38 years after the securing of the specimen and after it is completely dried up.

Humidity and temperature may, even *in vitro*, exercise specific influences on the cluster forms.

It is probable that the soil bacterial clusters may be considered as "cysts" functionally analogous to those of the protozoa.

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EFFECT OF DROUTH ON THE NUTRIENT LEVELS IN THE TOMATO PLANT[1]

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Received for publication June 27, 1935

Previous tests on the tomato plant (2) showed that plants grown in a dry soil accumulated nitrate nitrogen, showed a marked lowering of phosphate phosphorus, and gained in percentage of potassium. That work was done in pots with controlled moisture. In the present work the tomato plants were grown in regular greenhouse raised benches of 8-inch depth, giving the plants a spacing of 2 feet each way. This experiment was conducted to check the previous work under more practical conditions and to obtain further data on the reliability of the plant tests as indicators of available nutrients in the soil.

PROCEDURE

Six plants were set in each of two soil types, a red clay soil and a black silt loam. The spacing and arrangement (fig. 1) were the same for both soil types used.

Just enough water was supplied to the dry section to keep the plants from wilting during normal weather conditions. On bright days, the plants wilted, but not enough to prevent ready recovery. Enough moisture was applied to the wet section to keep the soil well moistened at all times. Excessive moisture could not collect, since a loose cypress bottom permitted ready drainage. The plants were all watered at the start until they were about a foot high, when water was reduced on the dry sections.

Samples for analysis were taken from the lower mature petioles of the plants in the wet and dry sections containing two plants each. The two plants in the medium section served merely as buffer plants. Samples from the dry plots were never taken when the plants were actually wilted. The analyses were conducted by methods previously described (1). For accurate work, a 5-gm. sample was extracted with 50 cc. of 2 per cent acetic acid instead of 10 cc. as in the field tests (1). Of this extract, 5 cc. was used for nitrate nitrogen, 10 cc. for phosphate phosphorus, and 25 cc. for potassium. A Bausch and Lomb colorimeter was used to make the color comparisons.

[1] The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.

RESULTS

Nitrate nitrogen

Table 1 shows that a definite concentration of nitrate nitrogen in the plants on the dry plots took place. The differences between the nitrate in the plants on dry and wet plots were greatest toward the end of the experiment. Evidently, on the dry plot, the lack of water and likely the decrease in phosphate percentage caused a lack of nitrate utilization and consequent accumulation. Apparently, the plant was able to get nitrate from the dry soil. However, nitrate absorption may have been retarded, the lack of utilization making it appear that the plant was still absorbing a large amount of nitrate.

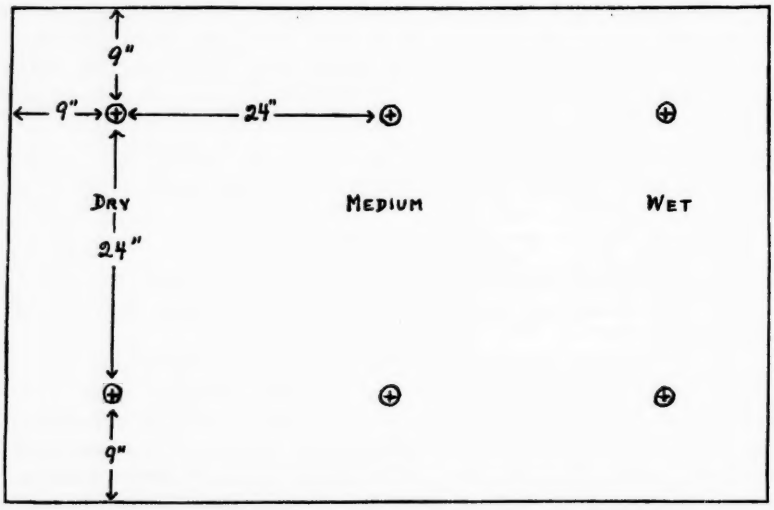

FIG. 1. SPACING AND ARRANGEMENT OF THE SIX TOMATO PLANTS IN THE GREENHOUSE BENCH

The tests also plainly show that the black silt loam was much more capable of supplying nitrate than was the red clay. The plants in the red clay soil were much smaller on both the dry and wet sections than were those on the black silt loam. The plants on the dry plots of both soil types showed the characteristic dark green color of plants containing much nitrogen and were greatly stunted. The plants on the wet plots looked normal and bore a fair crop of fruit, whereas the fruits on the plants in the dry plots were small, and practically none matured without blossom-end rot being present.

Phosphate phosphorus

A decrease in the concentration of phosphate in plants on the dry plots is apparent from table 2. At the time of the first and second samplings, Octo-

ber 26 and 29, plants in the dry red clay soil did not show a reduction of phosphate, whereas the black silt loam, although causing a much higher level of phosphate, showed a lower phosphate level in the plants on the dry soil at all times. Water was withheld about a week before the first sampling, but the dry plots had been dry only several days before the samples were taken. The proportion of phosphate was noticeably smaller in the plants in the dry red soil at the time of the third sampling, on November 7, and continued to decrease. On December 9, the diminution was much more marked than that caused on the dry black silt loam.

TABLE 1

Nitrate nitrogen in plants grown on wet and dry plots

(p.p.m. of fresh tissue)

TREATMENT	SOIL	OCT. 26	OCT. 29	NOV. 7	NOV. 12	NOV. 18	NOV. 28	AV. IN OCT.	AV. IN NOV.	DEC. 9
Dry.....	Black silt loam	1,408	1,146	1,210	917	555	422	1,277	776	714
Wet.....	Black silt loam	578	742	1,180	373	90	224	660	467	14
Dry.....	Red clay	122	49	176	45	35	29	86	71	23
Wet.....	Red clay	44	52	51	34	22	15	48	31	0

TABLE 2

Phosphate phosphorus in plants grown on wet and dry plots

(p.p.m. of fresh tissue)

TREATMENT	SOIL	OCT. 26	OCT. 29	NOV. 7	NOV. 12	NOV. 18	NOV. 28	AV. IN OCT.	AV. IN NOV.	DEC. 9
Dry.....	Black silt loam	273	431	275	218	114	122	352	182	214
Wet.....	Black silt loam	385	478	376	334	178	182	432	268	333
Dry.....	Red clay	69	57	43	19	25	35	63	31	19
Wet.....	Red clay	69	52	52	24	53	52	61	45	77

Some may raise the point that the plants were stunted on the dry soil and that this would cause a change in cell sap. A lack of water should concentrate the cell sap. Previous work (2), however, shows that this increase in concentration is small. It might be that a small increase in nutrients could be accounted for by the stunting effect, but in the case of phosphorus there is a decrease despite any increase in sap concentration which may have occurred. A small part of the nitrate increase may be caused by the increased concentration of cell sap but this could hardly be responsible for the large nitrate increase found. The difference in the ability of the two types of soil to supply phosphorus to the plant is brought out consistently and strikingly by the results of the plant tests in table 2.

This decrease in the phosphate level in plants in the dry soils undoubtedly was due to a lack of availability of phosphorus in the dry soil. Since the vigor-

ous plants growing in the rich black soil almost immediately showed a reduced phosphate content, the decrease could hardly be ascribed to a lack of vigor in the roots. The roots evidently continued to send up nitrate and potassium, which also would show that the roots were still vigorous in nutrient uptake, but it seems reasonable to conclude that they were unable to extract as much phosphate from the dry soil as they did from the wet soil.

Potassium

Table 3 shows a consistent increase in the concentration of potassium in the plants grown in the dry soils. Just why this is the case is hard to say, but only a small part of this is likely to have been due to increased concentration of cell sap, since the water content of sap is only 1 to 2 per cent below that of plants on wet soils, as previously shown (2). The difference in the amount of potassium maintained by the two soil types is slight, the rich black soil maintaining a slightly higher amount in most cases. The fact that the concentration of potassium in plants on the black soil dropped below that in plants

TABLE 3

Potassium in plants grown on wet and dry plots

(p.p.m. of fresh tissue)

TREATMENT	SOIL	NOV. 12	NOV. 18	NOV. 28	AV. IN NOV.	DEC. 9
Dry	Black silt loam	3,200	3,360	4,600	3,720	3,760
Wet	Black silt loam	2,800	2,620	3,380	2,933	2,800
Dry	Red clay	2,560	3,160	4,200	3,307	3,856
Wet	Red clay	2,016	2,480	3,340	2,612	3,800

on the red soil in December may be ascribed to the translocation to the larger number and much larger size of fruits on the plants on the black rich soil.

Reliability of field tests

Since the data reported here were obtained in a way similar to field tests for nitrate, phosphate, and potassium previously described (1), the difference being only in the amount of solvent used and the method of matching colors, it is apparent that these data give further proof of the reliability of these tests. The data are consistent in showing a reduction in phosphate and increases in nitrate and potassium on dry soils. They are also consistent in showing the differences in level of nutrients in the plant maintained by the two different types of soil used.

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SOIL REACTION AND AZALEA GROWTH

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Received for publication May 6, 1935

The azalea plant is recognized as belonging to a group of plants that require an acid soil reaction for their best growth. Thus Wilson and Rehder (8) point to the abundant occurrence of azaleas on the volcanic mountains of Japan in the absence of limestone, a condition favorable for the growth of the members of the family Ericaceae. Cox (2), in discussing the growth of the rhododendron, emphasizes that these plants prefer a soil with a certain amount of acidity, commonly provided by decaying vegetable matter. Wilson (7) warns the grower of azaleas that this plant demands a lime-free soil. Wherry (6) lists azaleas and rhododendrons as plants preferring or even requiring "subacid" soils. He designates "subacid" as a range between pH 5.1 and 6.0. Ward (5) emphasizes the fact that rhododendrons require an acid soil which is thoroughly impregnated with decomposing organic matter. Barron (1) lists azaleas as plants that will not tolerate alkaline soils. Hume (3) writes: "In common with the rhododendron, mountain laurel, andromeda, blueberry and tar flower, to which they are closely related, azaleas are acid-soil inhabiting plants. They are intolerant of lime and will not grow satisfactorily in alkaline soils or those in which lime is present in any appreciable amounts." Spencer (4) in his studies of the distribution of *Rhododendron maximum* in New Jersey did not find these plants on soils with a reaction above pH 5.6.

These reports furnish abundant evidence that the azalea plant and the closely related species require an acid soil for healthy growth. However, despite the increased use of these plants as ornamentals, neither the growth response of the plant to different degrees of soil acidity nor the type of injury attributable to alkaline soils has been studied extensively under controlled conditions. This paper reports a series of studies on the growth response of the azalea plant (*Azalea indica*) at different degrees of soil acidity and a survey of the reaction of the soils of azalea plantings of both the Indian and Kurume groups in a few of the southeastern states.

GROWTH RESPONSE AND SOIL REACTION

Controlled cultural experiments with azaleas were started in the fall of 1931. A sandy soil with a relatively low content of organic matter and an original

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pH value of 5.76 was adjusted to different degrees of acidity by the addition of sulfuric acid or calcium carbonate. The range of soil reaction selected for study was from approximately pH 4.50 to approximately pH 8.00. Preliminary laboratory trials indicated the quantities of sulfuric acid or calcium carbonate required to obtain the desired degrees of acidity or alkalinity. The acid-treated soils were leached with tap water in the establishment of the equilibrium between the acid and the soil. By means of periodic determinations of the H-ion concentrations, the change in soil reaction was followed through the course of the experiment. Aluminium sulfate was used in an attempt to keep the acid range intact, but its use did not prevent the occurrence of an appreciable variation in the range of the H-ion concentration during the course of the experiment. The quinhydrone electrode was used to determine the H-ion concentrations in a 1–2 soil-distilled water suspension.

In October 1931, vigorous and apparently quite healthy azalea plants of the Indian group, Formosa variety, of uniform size and age, with the roots thoroughly cleansed of adhering soil, were planted in the soil in 4-gallon glazed pots. The pots contained 38 pounds of the soil, which had been adjusted in a series to different degrees of soil acidity. The cultures were kept in a half-shade slat shed during the course of the experiment, and were watered by the rain and by frequent applications of tap water. At intervals the plants were fertilized uniformly with liberal applications of cottonseed meal and tankage. Growth observations were made during the 2-year course of the experiment, which terminated in October 1933.

The plants were photographed at the termination of the experimental period, Plate 1, figure 1, demonstrates the outstanding response of the Formosa azalea plant to different degrees of soil acidity. The plants at the distinctly acid range were characterized by a slow growth and short stems between the whorls of branchlets, but the foliage was a healthy green; those at a soil pH of 6.23, by elongated growth with long stems between the whorls, and healthy green foliage; and the ones growing in a soil with an average pH of 7.58, by slow growth, distinct yellowing of the tissues between the veins of the leaves, narrow green areas of tissues along the veins, and a general unhealthy appearance indicative of a lack of thrift.

A bed of azaleas of the Formosa variety growing on the horticultural grounds of the Florida Agricultural Experiment Station was used as a correlation in definitely determining the limits of alkalinity which bring about the chlorosis of azalea plants. The soil was a Norfolk medium fine sand very similar to that used in the pot experiments. Accidently, through the dumping of spray materials, a range of reaction had been brought about in the soil in different parts of the bed, and the plants had grown under these conditions for several years.

Three distinct plant conditions, as shown in plate 1, figure 2, were found to exist in this bed. The sprig on the left was from a plant growing in a soil with a reaction of pH 6.52, the middle sprig with partially chlorotic foliage

was from one growing in a soil with a reaction of pH 7.07, and the sprig on the right was from one in a soil having a pH of 7.31. The distinctly chlorotic condition of the plant growing in a soil having a reaction of pH 7.31 should be emphasized. The green veins and the yellowed areas between are characteristic of azalea plants growing in a distinctly alkaline soil, containing carbonates. These results suggest that the danger zone, as far as chlorosis in azaleas caused by an alkaline soil is concerned, lies within the narrow limits of soil acidity represented by a pH range between 6.50 and 7.00.

These field studies, combined with the pot cultures as described, give a basis for a more definite determination of the growth response of azaleas to the different degrees of soil acidity.

Plate 1, figure 3, shows the entire series of pot cultures and indicates the growth response in the Formosa variety that may be expected at different degrees of soil acidity. Growth was slow, and both the stem length and the internodes between the whorls of branches were definitely shortened at a soil pH value lower than 5.00. However, the foliage was dark green and the plants appeared healthy and flowered normally. With the Formosa variety, and perhaps others, it appears that the soil acidity should be kept below pH 5.00 where low-growing, bunchy plants are desired. An intermediate type of growth was observed between pH 5.00 and 6.00. Here, the stems between the whorls of twigs were elongated, and twig growth was lengthened. This condition produced a larger but yet not spreading plant, which without doubt is suitable for many uses in the garden. The foliage was healthy and green and the flowering normal in this range. Within a soil reaction range represented by a pH value of about 6.00 to slightly above a pH value of 6.50, the growth was rapid with distinctly elongated stems between the whorls of branches. This condition resulted in an open, somewhat sprawling type of plant. Foliage was healthy and flowering normal. Above a soil reaction of pH 7.00, shortened growth with distinctly chlorotic leaves, sparse foliage, and a general unhealthy plant condition were observed. In this range the plants flowered sparsely. The range of reaction represented by pH values between 6.50 and 7.00 may be considered a danger zone in which azalea plants, although not without exception, are likely to become chlorotic.

The response of these azalea plants to different degrees of soil acidity under controlled conditions made a survey of the soil reaction of azalea plantings of particular interest. Such a survey was undertaken during the winter and spring of 1933–34.

SURVEY OF THE REACTION OF THE SOILS OF AZALEA PLANTINGS

As it was not feasible to visit and sample the soils of the numerous azalea plantings, requests were made of a number of friends and growers of azaleas to collect soil samples and forward them to Gainesville, where the H-ion determinations were made. Table 1 gives the names of the areas sampled, the number of locations sampled, and the number of samples taken. In all, 21

areas, 63 locations, and 168 azalea soils were sampled. Samples from the famous planting in the Magnolia Gardens at Charleston, S. C., as well as from the oldest plantings in Florida were included. Several soil samples also were taken from wild species.

As a rule the samples were taken to a depth of 12 inches—a soil depth which probably contains the greater portion of the root systems of the plants. The samples were collected underneath the growing plants. Since the soil samples were collected from different depths by the various collectors, the H-ion concentrations of the different depths have been averaged for any one soil. All

TABLE 1

List of areas where soil samples from azalea plantings were collected

AREA	LOCATIONS	NUMBER OF SAMPLES
Charleston, S. C.	2	19
Savannah, Ga.	2	3
Macon, Ga.	1	1
Mobile, Ala.	4	9
Marianna, Fla.	1	2
Quincy, Fla.	4	4
Tallahassee, Fla.	2	6
Monticello, Fla.	5	18
Lake City, Fla.	1	3
Glen Saint Mary, Fla.	5	10
Jacksonville, Fla.	7	15
Hastings, Fla.	1	3
St. Augustine, Fla.	2	2
Deland, Fla.	3	9
Gainesville, Fla.	5	6
Leesburg, Fla.	3	8
Tampa, Fla.	1	6
Bradenton, Fla.	1	1
Winter Park, Fla.	3	6
Winter Haven, Fla.	3	25
Lake Wales, Fla.	7	12
Totals 21	63	168

H-ion concentrations were determined in the same manner as used for the pot experiments. It was impossible to designate the different soil types, as in a majority of the cases the soils had been especially prepared for azalea culture by additions of mucks or other soils and vegetable litter.

The results of the determinations of the pH values of the azalea soils are shown graphically in figure 1. The graph illustrates the distribution of these soils with regard to soil reaction. As may be noted, the greatest number (38.7 per cent) of the azalea soils were found to have a pH value between 5.00 and 6.00, a range of H-ion concentration evidently very favorable for

the growth of azalea plants. In 67.8 per cent of the soils the reaction was lower than pH 6.00. In 26.8 per cent of the samples the reaction was between pH 6.00 and 7.00. Of these last-named samples, 16.7 per cent were found to be between pH 6.00 and 6.49, and 10.1 per cent were found in the range of pH 6.50 to 6.99, a range previously designated as the danger zone for chlorosis. In all, 15.5 per cent of the soils were in the zone of possible injury from chlorosis, and 29.1 per cent of the plants were growing in very acid soils (lower than pH 5.00). The most acid soil had a pH value of 3.54; the most alkaline,

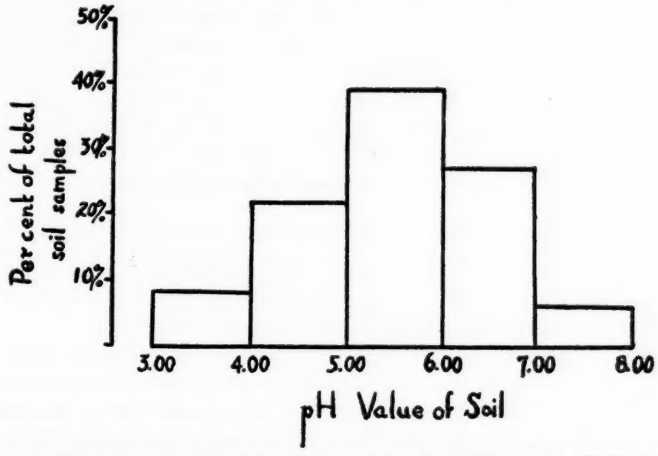

FIG. 1. DISTRIBUTION OF SAMPLED AZALEA SOILS WITH REGARD TO pH VALUES

TABLE 2

Reported condition of azalea plants at different degrees of soil acidity

PLANT CONDITION	pH RANGE OF SOILS					
	3.00–4.00	4.00–5.00	5.00–6.00	6.00–6.50	6.50–7.00	7.00–8.00
Number of soils sampled	12	37	65	28	17	9
Percentage of plants reported healthy	75	76	75	71	47	22
Percentage of plants reported unhealthy	25	24	25	29	53	78

a value of 7.48. The acid soil was collected from a drained cypress swamp; the alkaline soil, near a building where lime materials had accumulated. Observations on the growth condition of the plants were made at the time the soil samples were collected.

The notes on plant thrift are summarized in table 2, where the percentages of healthy and of unhealthy plants are given for each reaction range of the soil. From the table it may be seen that up to a soil pH value of 6.50, approximately 75 per cent of the azalea plants were reported in a healthy condition.

The range of soil pH values between 6.50 and 7.00 is marked by an abrupt change of plant condition, wherein only 47 per cent of the plants were reported to be healthy. Above a soil pH value of 7.00 only 22 per cent of the plants were reported as being in a thrifty condition—in other words, two only of the nine sampled. In this last range, the two samples of soils reported from healthy azalea plants were from specimens growing in a soil with a pH value of 7.20—slightly above the neutral point. Where a soil reaction above pH 7.00 was accompanied by an unhealthy plant condition, the plants in every instance were reported as being chlorotic. Many of the plants growing on soils with a reaction between pH 6.50 and pH 7.00 were reported as chlorotic. The rapidity with which transplanted azalea plants are affected by soil reaction apparently is in direct ratio with the degree of acidity or alkalinity of the soils in question. Thus on a soil with a nearly neutral reaction, plant vigor would be more slowly checked than on a strongly alkaline one, highly alkaline soils reacting adversely within a comparatively short time. The results of this survey corroborate those obtained in the control experiments.

SOME ADDITIONAL FACTORS AFFECTING AZALEA GROWTH

Factors other than soil reaction were reported as bringing about an unhealthy growth of the azalea plant. A few of these factors and their effects on the growth of the azalea plant will be briefly discussed.

Poor Soil Drainage.—Although the azalea is recognized as a plant that requires a great deal of water for its growth, it cannot be considered as one that will grow in a poorly drained soil. Several instances of plants suffering from poor drainage were reported in the survey of the soils of azalea plantings. In one instance where the water table was only 10 inches below the surface, the plant had an appearance not unlike those affected with lime chlorosis, although the soil was sufficiently acid in reaction. Small leaves with yellow areas between the veins were observed, and the plant was definitely stunted in growth. In other instances of excessively poor drainage, plants were reported as being virtually killed by the suffocation of the roots in the saturated soils.

Drought.—A distinct curtailment of the water supply first causes extreme wilting of the foliage and soon brings about a dying back of twigs and a definite lack of thrift in the plant. In common with numerous plants growing in humid regions, the azalea seemingly to a degree adjusts itself to a limited supply of water by a corresponding limitation of root and top growth but suffers acutely from extended periods of little moisture. Several instances of drought injury were reported in the survey.

Fertilization.—An unhealthy plant condition brought about very likely by inadequate fertilization was observed in the survey. A very light green foliage, which is commonly characteristic of an insufficiency of nitrogen in many plants, was noted in several instances. The azalea plant usually is greatly benefited by liberal applications of commercial fertilizing materials, which in most cases

should be from sources that will tend toward the creation of a more acid soil condition.

Cold Damage.—Symptoms of cold injury are in nowise similar to those due to an unsuitable soil reaction and there is little likelihood of confusing the two. Frost injury may not be apparent until after a lapse of several weeks from the time of the actual freezing and may be characterized by rather sudden wilting of the foliage on a twig, branch, or even the whole plant, followed by a browning of the leaves and later death of the affected parts.

SUMMARY

1. Formosa azalea plants were grown in a soil adjusted to different degrees of soil acidity. Below a degree of acidity represented by pH 5.00, the plants made a slow but healthy growth under the conditions of these experiments. Between pH 5.00 and 7.00, the plants made a vigorous, healthy, elongated growth. The plants grown between pH 5.00 and 6.00 were especially healthy with desirable growth characteristics. Above pH 7.00, the growth was slow and the foliage chlorotic.

The chlorosis of the azalea which is produced by an alkaline soil may be described as a yellowing of the tissue of the leaves between the veins. The veins remain green. Chlorotic leaves are usually smaller than healthy green leaves.

2. A survey of azalea soils included 168 samples of soil taken from the first foot of azalea plantings in several southeastern states. Of the soils, 94.6 per cent had pH values lower than 7.00. The range of pH values between 5.00 and 6.00 had the largest number of the samples (38.7 per cent). Approximately 75 per cent of the plants were reported healthy when the soils had a pH value lower than 6.50; 47 per cent of the plants were reported healthy in a pH range between 6.50 and 7.00; and only 22 per cent were reported healthy when the pH value of the soils exceeded 7.00. The chlorosis induced by an alkaline soil was responsible for the lack of thrift in the majority of the unhealthy plants reported for soils with pH values above 7.00.

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PLATE 1

Effect of Soil Reaction on Growth and Foliage of Azalea

Fig. 1. The outstanding growth responses of the Formosa azalea plant to different degrees of soil acidity. Uniform plants set October 1931; photographed October 1933.

Left—average pH 4.78; slow growth; stems between whorls shortened; foliage green; flowering normal.

Middle—average pH 6.23; more rapid growth; stems between whorls elongated; foliage green; flowering normal.

Right—average pH 7.58; slow growth; practically all leaves chlorotic; flowering sparse.

Fig. 2. Limits of alkalinity bringing about a chlorotic condition of azalea foliage on a sandy soil.

Left—green foliage. Five soil samples, average at depths of 0–2 inches, pH 6.39; 2–6 inches, pH 6.63; 6–12 inches, pH 6.64; average all depths, pH 6.52.

Middle—partially chlorotic foliage. Four soil samples, average at depths of 0–2 inches, pH 7.04; 2–6 inches, pH 7.07; 6–12 inches, pH 7.11; average all depths, pH 7.07.

Right—chlorotic foliage. Three soil samples, average at depths of 0–2 inches, pH 7.34; 2–6 inches, pH 7.36; 6–12 inches, pH 7.29; average all depths, pH 7.31; carbonates present in all samples.

Fig. 3. Growth response of the Formosa azalea to different degrees of soil acidity. Plants of uniform size and age set October 1931; photographed January 1934.

	1	3	4	5	6	7	8	9	10	11	12	13	14
Average pH.....	4.78	4.82		5.65		6.23		6.49		6.61		7.58	
Average spread...	44 in.	41 in.		52 in.		58 in.		52 in.		57 in.		35 in.	
Average height...	25 in.	34 in.		38 in.		37 in.		42 in.		31 in.		28 in.	
	Range of slow growth. Bunchy plants. Healthy green foliage Natural flowering			Range of elongated growth—usually more elongated under less acid conditions. Healthy green foliage. Natural flowering						Range of danger of lime chlorosis		Range of slow growth and chlorotic foliage. Sparse flowering	
pH.....	3.00			5.00						6.50		7.00	8.50

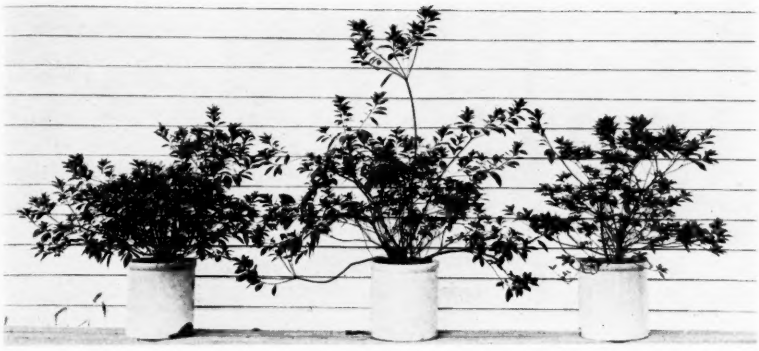

FIG. 1

FIG. 2

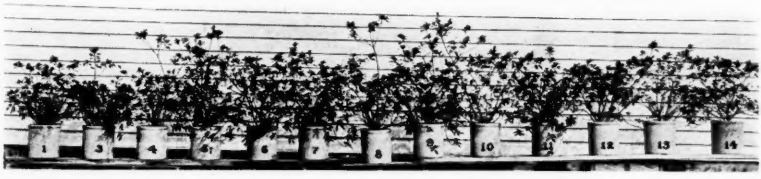

FIG. 3

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